Aalto-yliopisto
Insinööritieteiden
korkeakoulu

Anna Gulkova

# Evaluation of water treatment methods and identification of the best available technology for Kristineberg mine area

Master's thesis for the degree of Master of Science in Engineering submitted for inspection.

Espoo 18.02.2018

Supervisor: Prof. Riku Vahala

Instructors: D.Sc. Jari Aromaa, M.Sc. Ksenia Novikova

Aalto-yliopisto
Insinööritieteiden
korkeakoulu

Aalto University, PL 11000, 00076 AALTO

www.aalto.fi

**Abstract of Master's thesis**

| | | |
|---|---|---|
| **Author** Anna Gulkova | | |
| **Title of the thesis** Evaluation of water treatment methods and identification of the best available technology for Kristineberg mine area | | |
| **Degree programme** Water and Environmental Engineering | | |
| **Major/minor** Water and Environmental Engineering | | **Code** ENG29 |
| **Thesis supervisor** Prof. Riku Vahala | | |
| **Thesis instructors** D.Sc. Jari Aromaa, D.Sc. Ksenia Novikova | | |
| **Date** 18.02.2018 | **Number of pages** 75+19 | **Language** English |

**Abstract**

Mining of pyrite-rich ore deposits produces large volumes of acid mine drainage, which has low pH and high concentrations of heavy metals and sulfates. Upcoming Swedish environmental regulations aim to decrease maximum allowed concentrations of metals in water discharged to natural water bodies. Conventional processes are not able to achieve the upcoming requirements, which leads to demand for new solutions. This thesis identifies water treatment methods that could potentially be used to treat mine drainage from Kristineberg mine in northern Sweden to comply with the proposed requirements. This work evaluates chemical methods of acid mine drainage treatment with particular focus on precipitation of metals as hydroxides and sulfides. Co-precipitation and adsorption of metals by ferric hydroxide and manganese dioxide as polishing step after neutralization were also investigated. The work was done by modelling and laboratory experiments with mine drainage obtained from Kristineberg mine area.

It was found that neutralization of mine drainage and hydroxide precipitation of metals could not reach the proposed requirements for arsenic and copper. Applying Fenton reagent and manganese oxidation as a polishing step improved removal of all metals, but residual As and Cu concentrations were still slightly higher than required. Sulfide precipitation of metals after removal of iron and aluminium as hydroxides showed better removal of copper, but removal of nickel was not achieved. Removal of uranium was also worse than that achieved by neutralization. However, because sulfide precipitation produces less sludge and makes metals recovery possible, the study concluded that it is a more attractive option for Kristineberg mine drainage treatment. But additional studies are required to find optimum conditions for nickel removal. Conducting bench-scale experiments with hydrogen sulfide gas as a sulfide source is recommended.

The study found that both neutralization with polishing and sulfide precipitation would reach lower effluent metal concentrations than those reached by the existing Kristineberg water treatment plant. But it was concluded that the proposed discharge requirements are unrealistically low, especially for As, and it is likely that a full-scale water treatment plant would not be able to consistently reach these limits for all the specified metals.

**Key words** acid mine drainage, water treatment, metals solubility, hydroxide precipitation, sulfide precipitation, Fenton reagent, modelling

**Author** Anna Gulkova

**Title of thesis** Utvärdering av vattenreningsmetoder och identifiering av bästa vattenrening teknik för Kristineberg gruvområde

**Degree programme** Vatten och Miljö teknik

**Major/minor** Vatten och Miljö teknik **Code** ENG29

**Thesis supervisor** Prof. Riku Vahala

**Thesis advisor(s)** D.Sc. Jari Aromaa, D.Sc. Ksenia Novikova

**Date** 18.02.2018 **Number of pages** 75+19 **Language** Engelska

**Referat**

Utvinning av pyrit-rika malm producerar stora mängder av surt gruvvatten, som har lågt pH och höga koncentrationer av tungmetaller och sulfat. Nya svenska miljöföreskrifter strävar efter att minska maximalta tillåtna metallkoncentrationer i vatten som släpps ut i naturliga vattendrag. Konventionella processer kan inte möta de kommande kraven, vilket leder till en efterfrågan på nya processlösningar. Det här examensarbetet identifierar vattenbehandlingsmetoder som potentiellt kan användas för att behandla gruvvatten från Kristinebergsgruvan i norra Sverige för att kunna följa de föreslagna kraven. Det här arbetet utvärderar kemiska metoder för behandling av surt gruvvatten med särskild inriktning på utfällning av metaller som hydroxider och sulfider. Samutfällning och adsorption av metaller med järnhydroxid och mangandioxid som poleringssteg efter kalkning undersöktes också. Arbetet gjordes genom modellering och laboratorieexperiment med gruvvatten från Kristinebergsgruvan.

Det konstaterades att kalkning av gruvvatten och hydroxidutfällning av metaller inte kunde möta de nya kraven för arsenik och koppar. Men med hjälp av Fenton-reagens eller manganoxidation som ett poleringssteg förbättrades avlägsnandet av metaller. Användning av sulfidutfällning av metaller efter borttagning av järn och aluminium som hydroxider visade bättre utfällning av koppar, men nickel-kravet uppnåddes inte. Avslängande av uran var också sämre an med kalkning av gruvvatten. Men eftersom sulfidutfällning producerar mindre mängder av slam och gör det möjligt att återvinna metaller, konstaterades att det är ett mer attraktivt alternativ för behandling av det sura vattnet från Kristinebergsgruvan. Men ytterligare studier krävs för att hitta optimala förhållanden för att ta bort nickel. Genomförande av experiment i bänkskala med vätesulfidgas som sulfidreagens rekommenderas.

Studien visade att både neutralisering med poleringssteg och sulfidutfällning skulle nå lägre metallkoncentrationer än de som nås i det befintliga vattenreningsverket i Kristineberg. Sammanfattningsvis konstaterades att de föreslagna utsläppskraven är orealistiskt låga, särskilt för As. Mest troligt kommer det blir svårt i en fullskalig anläggning att ständigt möta utsläppskraven för alla specifika metaller.

**Keywords** surt gruvvatten, vattenrening, metaller löslighet, hydroxidfällning, sulfidfällning, Fenton-reagens, modellering

# Preface

This thesis was done for Process Technology Department of Boliden Mineral AB as a part of my Master's degree in Water and Environmental Engineering at Aalto University.

For the possibility to work with this interesting topic I thank Andreas Berggren, the chief of Process Technology Department, who gave me the opportunity to conduct this project.

I would like to thank my instructor Ksenia Novikova from Boliden Mineral AB, who was guiding and supporting me through the course of this work. I would also like to thank Amang Saleh for advising me during laboratory work and Peter Lundell, who greatly helped me with analysis of samples. I would also like to thank Jan-Eric Sundkvist and Paul Kruger for inspiring me with ideas and offering practical advices.

I am glad to have had the opportunity to work along with all the people from Process Technology Department of Boliden Mineral AB. It has being a wonderful experience for me and I am thankful to everyone for help and support.

From Aalto University I would like to thank my instructor Senior Lecturer Jari Aromaa and my supervisor Prof. Riku Vahala for their advices on the thesis report and for examination of the final work.

Espoo 18.02.2018

*Anna Gulkova*

# Table of Contents

# List of tables

# List of figures

# List of terms and abbreviations

| | |
|---|---|
| AMD | Acid mine drainage |
| AOP | Advanced oxidation process |
| BOD | Biological oxygen demand |
| COD | Chemical oxygen demand |
| DOE | Design of experiments |
| Ettringite process | Sulfate removal process based on ettringite precipitation |
| EU WFD | European Union Water Framework Directive |
| HDS | High Density Sludge process |
| ICP-OES | Inductively coupled plasma optical emission spectrophotometer |
| LDS | Low Density Sludge process |
| PLS | Partial least squares model fit method for complicated applications |
| RO | Reverse osmosis membrane treatment process |
| TDS | Total dissolved solids |
| WTP | Water treatment plant |

# 1 Introduction

## 1.1 Background

Mining operations play an important role in development of our society, as currently mining products are used in nearly all industries. The demand for building materials, metals, and precious stones is constantly growing, leading to an increase in the number of mines. This has an effect on the natural environment, as often mining operations produce large volumes of wastewater and acid mine drainage (further AMD). AMD is typically formed due to oxidation of pyrite-rich ores. It is characterized by low pH and high concentration of sulfate and ferrous ions [1]. In Europe the European Water Framework Directive aims to control and prevent pollution of natural water bodies and aquatic ecosystems. The Directive obliges mining companies to treat wastewater before discharging it into the natural environment. The requirements are getting more stringent, and companies have to invest in new technologies to comply with the environmental regulations. Hence, operational costs of water treatment and fines for incompliance could have a significant impact on profitability of mining companies. Therefore, mine drainage treatment methods should be carefully selected to comply with environmental regulations and to avoid financial losses. There is also another reason to treat mine drainage: it contains high concentrations of valuable metals. Treatment processes could help recover these metals and turn them into products, which could off-set the treatment expenses [1]. Moreover, treatment of mine water could help mining companies to create positive image of their business, improve environmental and social conditions for local communities, and get social licence to operate.

## 1.2 Client and motivation

The master's thesis research work was done for Boliden Mineral AB during a period from 1st September 2017 until 19th February 2018. The research focused on finding the best available technology for AMD treatment from underground Kristineberg mine in Boliden area, Sweden. The mine produces complex sulphide ores, which contain zinc, copper, lead, gold, and silver [2]. Exploration is being conducted in the Kristineberg area [3], so mine could be expanded in the future, which would require construction of a new water treatment plant and/or extending capacity of the existing one, because it currently operates at maximum capacity. Furthermore, current level of metals removal would not be sufficient if proposed new discharge requirements are enforced. Metals of the biggest concern are arsenic, cadmium, copper, and zinc.

## 1.3 Research objectives and methods

The main objective of this thesis was to find the best water treatment method for removal of metals from Kristineberg mine water and to determine whether it allows achieving environmental discharge limits that are proposed by Boliden Mineral AB as a basis for an environmental permit.

The research was limited to chemical precipitation of metals from AMD, and hence use of adsorbents, membrane filters, wetlands, and biological metals removal techniques is not addressed in the present work.

In order to select the most promising water treatment methods a literature review was conducted. First purpose of the literature review was to analyse the existing situation with mine water treatment at Kristineberg, which was done using materials of previous research conducted by Boliden Mineral AB. Several field visits were also done to acquire additional information about operation of the existing treatment plant. The second purpose of literature review was to identify treatment methods potentially suitable for implementation at Kristineberg. It was done by analysis of academic research, commercial solutions available on the market, and solutions that are currently in the pilot testing phase. The literature review was done using available materials of Boliden Mineral AB and Aalto library services. For review of commercial technologies marketing materials of water treatment companies were used and enquiries were made when necessary.

Potential treatment methods were selected based on their applicability to the local climate and ability to treat large water volumes with high efficiency and minimal costs. Modelling of metals solubility in the mine drainage was done using SolGasWater software to compare two chemical precipitation options, namely hydroxide and sulfide precipitation. A series of screening laboratory tests with potential treatment methods was conducted to select the most promising alternatives. The selected alternatives were tested in more elaborate laboratory experiments to establish their efficiency for metals removal from AMD. Experiments were done with water samples taken from inlet to Kristineberg water treatment plant. The screening tests samples were analysed using ICP-OES in laboratory of Boliden Mineral AB, and samples form main tests were sent to accredited external laboratory ALS Scandinavia.

# 2 Theory

This Section contains overview of the acid mine drainage chemistry and factors that affect its formation. It also presents short overview of several chemical methods that could be used for metals removal from AMD and describes some commercial technologies available for mine drainage treatment.

## *2.1 Acid mine drainage formation*

Mining of pyrite-rich ores or simply their exposure to water and air is the primary cause of acid mine drainage formation. Oxidation of pyrite ($FeS_2$) and pyrrhotite ($Fe_{(1-x)}S$, where x=0-0.25) causes release of hydrogen and sulfate ions, forming acidic water. The main reaction steps of pyrite oxidation are described by the following reaction equations [4]:

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$

$$Fe^{2+} + 0.25O_2 + H^+ \rightarrow Fe^{3+} + 0.5H_2O \quad (2)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3(s) + 3H^+ \quad (3)$$

Therefore, the net reaction of pyrite oxidation could be written as follows [5]:

$$FeS_2 + 3.75O_2 + 3.5H_2O \rightarrow Fe(OH)_3(s) + 2SO_4^{2-} + 4H^+ \quad (4)$$

However, reaction (2) is the rate-determining step and is pH-dependent. At acidic pH of about 2-3, which is characteristic for AMD, it proceeds extremely slowly. Therefore, AMD would not be such a widespread environmental issue if it was not for Fe-oxidizing bacteria, such as *Acidithiobacillus ferrooxidans,* which can increase speed of Fe oxidation by several orders of magnitude in acidic waters and even at near-zero temperatures [4], [5], [6]. Other sulfide-bearing minerals, such as sphalerite, galena, and chalcopyrite do not form acid during contact with air, as can be seen from the respective reaction equations below [4]:

$$ZnS + 2O_2 \rightarrow Zn^{2+} + SO_4^{2-} \quad (5)$$

$$PbS + 2O_2 \rightarrow Pb^{2+} + SO_4^{2-} \quad (6)$$

$$CuFeS_2 + 4O_2 \rightarrow Cu^{2+} + Fe^{2+} + 2SO_4^{2-} \quad (7)$$

However, ferrous ion released during oxidation of chalcopyrite could be oxidized by water and air according to reaction Equations (2) and (3), hence releasing hydrogen ion. Moreover, in presence of ferric iron in acidic conditions primary oxidation reactions of sphalerite, galena, and chalcopyrite are as follows [4]:

$$ZnS + 8Fe^{3+} + 4H_2O \rightarrow Zn^{2+} + SO_4^{2-} + 8Fe^{2+} + 8H^+ \quad (8)$$

$$PbS + 8Fe^{3+} + 4H_2O \rightarrow Pb^{2+} + SO_4^{2-} + 8Fe^{2+} + 8H^+ \quad (9)$$

$$CuFeS_2 + 16Fe^{3+} + 8H_2O \rightarrow Cu^{2+} + 2SO_4^{2-} + 17Fe^{2+} + 16H^+ \quad (10)$$

As could be seen from the Eqs. (8)-(10) above, one mole of sulfide-bearing mineral can produce 8 to 16 moles of hydrogen ion, which in turn could dramatically decrease pH of natural waters. Transport of such acidic water and its contact with other minerals could lead to dissolution and transport of toxic heavy metals from mining site to natural water bodies.

To sum up all of the above, it could be said that the following factors play a major role in formation of AMD:

a. Mineralogy of the site, soil permeability, and hydrogeological conditions;
b. Amount of precipitation and exposure area of minerals to water and air;
c. Temperature, pH, and dissolved oxygen concentration of water;
d. Bacterial activity.

## 2.2 Metals precipitation theory

This Section presents chemical methods of metals removal from water and their mechanisms. Firstly, this section describes chemical neutralization of AMD, currently the most widely used method of metals removal, which is also the most inexpensive and easy to operate. Then it presents information on removal of metals from water as sulfides, which, unlike neutralization, allows production of commercially valuable precipitate. Furthermore, this Section describes application of Fenton reagent and Mn oxidation as effective treatment methods for metals removal due to high sorption capacity of Fe and Mn oxides.

### 2.2.1 Neutralization

One of the most inexpensive and widely used methods of AMD treatment is chemical neutralization, which includes addition of alkaline neutralization agents to water for precipitation of metals as hydroxides at high pH. Neutralization agents commonly used for AMD treatment include hydrated lime, limestone, caustic soda, magnesia milk slurry, magnesite, and dolomite. Their chemical properties and approximate costs are shown in the Table 1 below:

*Table 1. Chemical properties and costs (2005) of some neutralization agents* [5].

| Neutralization material | Chemical formula | Saturation pH | Solubility in cold water, mg/l | EUR/Tonne neutralized acid |
|---|---|---|---|---|
| Limestone | $CaCO_3$ | 8-9.4 | 14 | 10-30 |
| Dolomite | $CaMg(CO_3)_2$ | 8-9.5 | 10-300 | 10-30 |
| Magnesite | $MgCO_3$ | 9.5-10 | 60-100 | NA |
| Quicklime | CaO | 12.4 | 1300-1850 | 90-200 |
| Hydrated lime | $Ca(OH)_2$ | 12.4 | 1300-1850 | 100-250 |
| Caustic magnesia | MgO | 9.5-10.8 | 1-50 | 200-400 |
| Mg hydroxide | $Mg(OH)_2$ | 9.5-10.8 | 1-50 | 270-430 |
| Soda ash | $Na_2CO_3$ | 11.6 | 75000 | 330 |
| Caustic soda | NaOH | 14 | 450000 | 470-600 |

Selection of the reagents should be based on various parameters, such as reagent cost, reagent consumption and neutralising capacity, required handling precautions, toxicity, desired pH level, reaction rate, produced sludge volume and quality. Limestone is the cheapest option, but due to reaction buffering by carbon dioxide it typically could not increase pH above 8. But its advantage is release of carbon dioxide gas and increase of alkalinity in form of bicarbonate ions. Small bubbles of carbon dioxide prevent passivation of limestone particles and improve its reactivity. There are two models that describe neutralization of acidic water by limestone, one described with Eqs. (11)-(12) and another with Eqs. (13)-(14) [7]:

$$CaCO_3 + H_2SO_4 \rightarrow CaHSO_4^+ + HCO_3^- \quad (11)$$

$$HCO_3^- + CaHSO_4^+ \rightarrow CO_2 + H_2O + CaSO_4(s) \quad (12)$$

$$CaCO_3 + 2H+ \rightarrow Ca^{2+} + H_2O + CO_2 \quad (13)$$

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^- \quad (14)$$

Hydrated lime is relatively cheap and can increase pH of solution above 12. Since one mole of $Ca(OH)_2$ contains two moles of $OH^-$ ion, less moles of it is required to neutralize AMD compared to caustic soda. But about 125% stoichiometric value of hydrated lime should be used to account for passivation effect of iron coating forming on $Ca(OH)_2$ particles. The lime neutralization reaction is shown by the Eqs. (15)-(16) below [7]:

$$Ca(OH)_2 + 2H^+ \rightarrow Ca^{2+} + 2H_2O \quad (15)$$

$$Ca(OH)_2 + Me^{2+}/Me^{3+} + (OH^-) \rightarrow Me(OH)_2/Me(OH)_3 + Ca^{2+} \quad (16)$$

However, important fact to consider is that $Ca(OH)_2$, $CaCO_3$, and $Mg(OH)_2$, unlike NaOH, are almost insoluble in water, and therefore should be dosed carefully to ensure good mixing and equal distribution throughout the solution volume. Poor mixing could result in local overdose or underdose of reagent, or decrease in effective reaction surface. However, advantage of these reagents compared to caustic soda is that unreacted particles have high adsorption capacity and could act as coagulants.

Main mechanism of neutralization treatment is increase of pH to precipitate metal hydroxides, whose solubility is a function of pH. However, co-precipitation and adsorption also play an important role in removing metals from water. They allow achieving lower effluent concentrations than those predicted by solubility products.

### 2.2.2 Sulfide precipitation

Sulfide precipitation of metals from AMD is based on the same principle as hydroxide precipitation – decrease of metal sulfides solubility with increase of pH. The main advantages of this process include much lower solubility product of metal sulfides at broader pH range, fast reaction, better stability of obtained sludge and its relatively low volume, possibility of selective metal precipitation and potential for recovery of metals from sulfide sludge. However, the disadvantages of sulfide precipitation include toxicity and difficulty of sulfide reagents handling, limited possibilities to control sulfide dosages, potentially harmful environmental effects of overdosing sulfide, difficulties in solid-liquid

separation due to small particle size of sulfides, and the fact that some metals, such as Fe, Al, and Cr do not form sulfides [8].

There are several options for dosing sulfide to AMD. Application of FeS is called insoluble sulfide precipitation (ISP). Since FeS is relatively insoluble it produces undetectable quantities of $H_2S$ gas, but disadvantage is larger than stoichiometric reagent consumption and large quantities of sludge generated due to ferrous hydroxide formation [9]. Application of $Na_2S$, NaHS, CaS, and $NH_4S$ as sulfide sources is called soluble sulfide precipitation (SSP), and can result in $H_2S$ gas formation [8], especially at low pH. Released sulfide reacts rapidly with dissolved metals, and due to high nucleation rate formed particles could be small and hard to filter out [9]. There are also some commercial organosulfide reagents available, such as TMT15®, Na3T™, METALSORB™, and Hydrex™ 6909. Application of gaseous $H_2S$ is also possible and has such advantages as better mixing and sulfide distribution, and easier process control.

The thermodynamic equilibria involved in metal sulphide precipitation could be expressed by Eqs. (17)-(18) below [8]:

$$H_2S \leftrightarrow HS^- + H^+ \; K_{p1} = \frac{[HS^-][H^+]}{[H_2S]} \quad pK_1=6.66 \tag{17}$$

$$HS^- \leftrightarrow S^{2-} + H^+ \; K_{p2} = \frac{[S^{2-}][H^+]}{[HS^{2-}]} \quad pK_2=17.4 \tag{18}$$

Figure 1 below illustrates dependency of sulphur species on pH of solution:

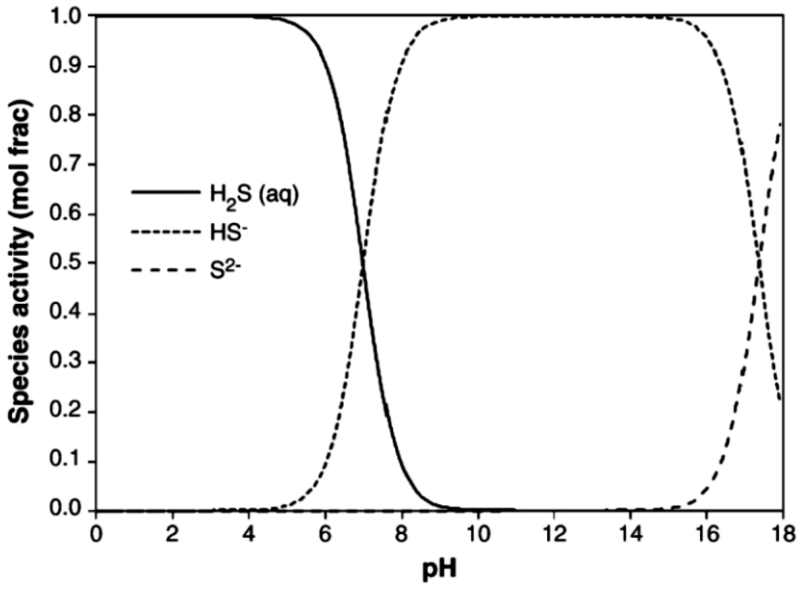


*Figure 1. Dependency of sulphur species activity on pH of solution* [8].

As could be seen from above, at different pH levels metals would react with sulfide either according to Eq. (19) or Eq. (20) below [8]:

$$M^{2+} + S^{2-} \leftrightarrow MS_{(S)} \tag{19}$$

$$M^{2+} + HS^- \leftrightarrow MS_{(S)} + H^+ \tag{20}$$

In Eqs. (19)-(20) $M^{2+}$ denotes such divalent metal ions as $Zn^{2+}$, $Ni^{2+}$, $Cu^{2+}$, and $Co^{2+}$. As could be seen from the reaction Equations (17)-(18) above, addition of $H_2S_{(g)}$ for metals precipitation causes release of protons and decrease of pH. However, addition of $Na_2S$ causes increase of pH according to Eq. (21) due to formation of sodium hydroxide [10], and by this analogy Eq. (22) could be written for pH increase during NaHS addition:

$$Na_2S + 2H_2O \leftrightarrow HS^- + H^+ + 2NaOH \quad (21)$$

$$NaHS + H_2O \leftrightarrow HS^- + H^+ + NaOH \quad (22)$$

Increase of pH with addition of $Na_2S$ was also reported by M. Ye *et al*. When large dosages of $Na_2S$ were added to the solution most of the reagent converted to $H_2S_{(g)}$, and only a small amount converted to $H_2S_{(aq)}$ or $HS^-$ [11].

### 2.2.3 Fenton reagent

Combination of hydrogen peroxide and ferrous iron is called Fenton reagent, after H. J. H. Fenton who discovered their combined oxidation effect in the end of 19$^{th}$ century [12]. It is considered to be one of advanced oxidation processes (AOP), or enhanced coagulation process, due to its characteristics described below. Hydrogen peroxide alone is a strong oxidant that has application in many fields, including removal of organic contaminants and water disinfection. However, its oxidation power could be further increased by using transitional metal salts, e.g. iron sulfate, as catalysts to induce decomposition of hydrogen peroxide and formation of hydroxyl radicals [13], [14]. The chemistry of Fenton reaction is complex, and despite numerous studies being conducted to determine the key oxidation species in the process, there is still no consensus [15]. But hydroxyl radical is commonly thought to be the main oxidant in the reaction chain. Its standard oxidation potential is 2.06 V, while for $H_2O_2$ this value is only 1.31 V [16]. The general mechanism of Fenton reaction in absence of organic compounds could be described using the following equations [12], [13], [17]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + OH^- \quad (23)$$

$$OH^\bullet + Fe^{2+} \rightarrow Fe^{3+} + OH^- \quad (24)$$

Formed ferric iron reacts with peroxide and catalyses it to decompose into water and oxygen as follows:

$$Fe^{3+} + H_2O_2 \rightarrow Fe\text{-}OOH^{2+} + H^+ \quad (25)$$

$$Fe\text{-}OOH^{2+} \rightarrow HO^\bullet_2 + Fe^{2+} \quad (26)$$

$$Fe^{2+} + HO^\bullet_2 \rightarrow Fe^{3+} + HO_2^- \quad (27)$$

$$Fe^{3+} + HO^\bullet_2\text{-} \rightarrow Fe^{2+} + H^+ + O_2 \quad (28)$$

$$OH^\bullet + H_2O_2 \rightarrow H_2O + HO^\bullet_2 \quad (29)$$

$$2HO^\bullet_2 \rightarrow H_2O_2 + O_2 \quad (30)$$

Simplified Fenton reaction accounting for dissociation of water has the following form [13]:

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O \quad (31)$$

The net reaction of Eqs. (23)-(30) of hydrogen peroxide decomposition catalysed by ferrous ion could be written as follows [15]:

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (32)$$

As can be seen from the Eq. (31) above, Fenton reaction requires hydrogen ions, and hence is favourable in acidic conditions. Generally, it is thought that pH in range of 3 is optimum [13], [15], [18]. In more acidic conditions regeneration of ferrous iron according to the Eq. (25) is inhibited. In more alkaline conditions ferric hydroxide precipitates and terminates the reaction, but acts as a coagulant. Due to this phenomena Fenton can play a double role, acting as oxidation and coagulation treatment steps simultaneously. One study reported that highest arsenate removal from synthetic mine drainage was achieved at pH 5 [14]. Ratio of reagents dosed also plays an important role in the process. At lower $H_2O_2/Fe^{2+}$ ratio Fenton acts more as a coagulation treatment, while at higher ratios the reaction has higher oxidation effect. Therefore, the main parameters that have to be controlled during Fenton reaction are concentration of reactants, pH level, and also temperature. Temperature increase improves kinetics of the reaction, but it also dramatically increases peroxide decomposition to oxygen and water at temperatures above 20 °C [18].

During ferric iron precipitation process co-precipitation, adsorption, and ion-exchange are important mechanisms of trace heavy metals removal from aqueous solutions. Adsorption is accumulation of metal ions on the surface of newly formed solid phase, while co-precipitation is the simultaneous removal of metal ions from solution during formation of iron precipitate. Co-precipitation may involve such processes as adsorption, cluster formation, homogeneous solid solution, heterogeneous solid solution, or their combination [19]. Since formed ferric hydroxide particles have low crystallinity, small size (in the range of micrometers to nanometers), and large specific surface area, they can efficiently adsorb dissolved metal ions [20]. It has been reported that As(V) is effectively removed from mine water by co-precipitation with schwertmannite or ferrihydrite, and to lesser extend due to adsorption [21]. It was also reported that schwertmannite is more effective than ferrihydrite for sorption of Pb, Cu and Zn, but they are equally effective for cadmium sorption. Removal of these metals is dependent on pH, with Pb being removed from the solution first, followed by Cu, Zn and Cd, and then Co [19]. Oxides of metals, including Fe, could also exhibit ion exchange properties. Ion exchange capacity of simple oxides exists due to presence of a pH-dependent surface charge. It has been reported that in acid solutions the surface charge is positive and therefore hydrous metal oxides could act as anion exchangers [22]. Because most of As in mine water is present in form of arsenate ($AsO_4^{3-}$), ferric hydroxide is a good scavenger of arsenic from water.

Multiple studies have been devoted to Fenton application for BOD and COD removal from landfill leachate [15], [23]. But limited amount of studies has been conducted on heavy metals removal from industrial waste water with Fenton or its application for AMD treatment [17]. However, mining wastewater typically has low pH and contains high concentrations of ferrous iron, which makes it suitable for application of Fenton. Moreover, advantage of Fenton compared to other AOPs is that no energy input is required to activate hydrogen peroxide, as the reaction takes place at atmospheric temperature and pressure. But one drawback of Fenton is relatively high cost of peroxide [18]. Hence, in recent decades a lot of interest has been attracted to unconventional Fenton processes

such as electro-Fenton [24], photo-Fenton [25], sono- and sono-photo-Fenton [26]. Research in this area aims to improve efficiency of Fenton treatment or decrease consumption of reagents required, therefore decreasing operational costs. Another drawback is large quantities of iron sludge produced during precipitation. This sludge also contains toxic metals, so special handling and disposal are required.

### 2.2.4 Manganese sulfate oxidation

Iron and manganese oxides play important role in controlling concentrations of metals in AMD and natural waters [19]. As was mentioned above, iron hydroxide is efficient for As removal due to having positive surface charge at low pH. In turn, manganese oxides, which precipitate at alkaline pH, have negative surface charge and thus higher affinity to divalent metal cations, such as $Cu^{2+}$, $Ni^{2+}$, and $Co^{2+}$, as well as $Zn^{2+}$ and $Cd^{2+}$ [19].

A significant number of studies has been conducted on heavy metals removal by natural manganese ores. Due to their high surface area manganese ores are widely used adsorbents. They are rather inexpensive and abandoned, and have shown high removal rates for such metals as Cu, Pb, Zn, and Cd [27], [28]. However, it has been found that freshly precipitated $MnO_2$ has a high sorption capacity for heavy metals, and that aging of precipitate is likely to significantly reduce this capacity. It was also found that effectiveness of heavy metal sorption by hydrous metal oxides depends on whether or not metals were present in the solution during precipitate formation [22]. Therefore, higher metal removal rates could be expected if $MnO_2$ precipitate formation occurs in the contaminated solution, compared to addition of $MnO_2$ as coagulant or adsorptive filter material. At alkaline pH and oxidizing conditions Mn(II) could be oxidized and form $MnO_2$ precipitate, though reaction kinetics is slow in water with pH below 8.5, and precipitation could take days. Increase of pH up to 10 is required for speeding up Mn(II) oxidation to time scale suitable for treatment plant operation, but reaching such high pH is not feasible. However, there are ways to increase the reaction rate. One option is to add catalytic surface, for example add solid $MnO_2$ to the solution [29]. Another method of achieving $MnO_2$ precipitate formation is pH adjustment of AMD to about 9 followed by addition of $MnSO_4$ together with an oxidizing agent, which would oxidize Mn(II) to Mn(IV) and produce $MnO_2$ precipitate. Optimum pH for this reaction is about 8.7, as at this pH $MnO_2$ has lowest solubility (around 0.02 mg/l) [30]. There are also biotic methods of Mn(II) precipitation, which are not discussed in the present work.

There are multiple oxidizing agents available on the market that could be used in water treatment and soil remediation for manganese oxidation, e.g. sodium persulfate ($Na_2S_2O_8$), sodium hypochlorite (NaClO), potassium permanganate ($KMnO_4$), and hydrogen peroxide ($H_2O_2$). The most widely used techniques for Mn precipitation and removal from water are aeration, ozonation, addition of permanganate, hypochlorite, or chlorine dioxide [31].

Persulfate is one of the strongest oxidants that is widely used for soil remediation. Theoretical standard oxidation potential of direct oxidation with persulfate is 2.0 V, according to the reaction as follows: $S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$ [32]. However, even though this reaction is thermodynamically favourable, it proceeds at a very slow kinetic rate. But apart from the direct oxidation, persulfate could also produce radicals. The two main radicals that are thought to be formed during in-situ chemical oxidation are produced as follows [32]:

$S_2O_8^{2-} + 2e^- \rightarrow SO_4^{2-} + SO_4^{\bullet-}$ (sulfate radical, potential 2.5-3.1 V [33]) (33)

$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + OH^{\bullet}$ (hydroxyl radical, potential 2.06 [16]) (34)

Activation of persulfate is commonly done using ferrous iron, but other transition metals could be applied as well [32], [34]. Due to reduction mechanism persulfate could be activated by metal ions or metal oxides as follows [33]:

$S_2O_8^{2-} + M^n \rightarrow M^{n+1} + SO_4^{\bullet-} + SO_4^{2-}$ (35)

Hypochlorite is the strongest oxidizing agent amongst chlorine oxianions, with a standard oxidation potential of 1.63 V. It reacts with Mn(II) according to the following reaction [30]:

$Mn^{2+} + 2OCl^- \rightarrow Cl_2 + MnO_2$ (36)

Potassium permanganate is widely used for Fe and Mn removal from water. It contains Mn in +7 oxidation state, which makes it a strong oxidizing agent with standard oxidation potential at alkaline conditions of 0.60 V. It reacts with Mn(II) according to the following reaction [35]:

$3Mn^{2+} + 2KMnO_4 + 2H_2O \rightarrow 5MnO_2 + 2K^+ + 4H^+$ (37)

As could be seen, the reaction requires alkaline pH, as it produces protons. It was reported that on practice less than stoichiometric amount of potassium permanganate is required (<1.92 mg/mg Mn) for Mn(II) oxidation, as formed $MnO_2$ precipitate catalyses the reaction [35]. This oxidation method is used in Veolia's MetClean$^{TM}$ process, described in the Section 2.3 Commercial methods.

As regards oxidation of Mn(II) by hydrogen peroxide, there is little data available. Some studies claim that $H_2O_2$ does not oxidize Mn(II) at pH range between 5.5 and 8.5 [29], [36]. Another study claimed in the presence of peroxide manganese could have oxidation states +2, +3, and +4. It was suggested that the reaction of Mn(II) oxidation in alkaline conditions in presence of peroxide follows Eqs. (38)-(42) presented below [37]:

$2Mn^{2+} + H_2O_2 \rightarrow 2Mn^{3+} + 2OH^-$ (38)

$4Mn^{2+} + O_2 + 2H_2O \rightarrow 4Mn^{3+} + 4OH^-$ (39)

$2Mn^{3+} \rightarrow Mn^{2+} + Mn^{4+}$ (40)

$Mn^{4+} + 2H_2O \rightarrow MnO_2 + 4H^+$ (41)

$MnO_2 + H_2O_2 \rightarrow Mn^{2+} + 2OH^- + O_2$ (42)

The oxidizing agents discussed above have their advantages and disadvantages. Addition of chlorine to mine drainage is general undesirable. If treated water is used as process water, presence of chlorine would cause corrosion of equipment. Chlorination residuals are also toxic for aquatic life. So increasing originally low levels of chlorine should be avoided. Initial concentration of sulfates in AMD is high, but addition of persulfate is also undesirable. Even though there currently are no requirements for discharge of sulfates, it is expected that they would come soon [38]. The disadvantage of permanganate is that

when overdosed it would give pink colour to the treated water. Ozonation is generally expensive, since ozone has to be produced on-site. Peroxide has a number of advantages. Hydrogen peroxide could be purchased, and residual products of its decomposition are water and oxygen gas. Therefore, it is an attractive option for an oxidant, as it does not produce secondary contaminants.

The disadvantages of using manganese oxidation for AMD treatment are similar to those of using Fenton reagent. Firstly, overdosing of metal reagent produces secondary contamination in the effluent. Overdosing oxidation agent is also dangerous for aquatic life. Secondly, the sludge produced has to be thickened and dewatered prior to disposal. Presently such sludge has no commercial application, but it might be profitable to leach it for metals recovery in the future.

## 2.3 Commercial methods of acid mine drainage treatment

There are various commercial technologies for mine water treatment available on the market, however, a wide range of them would not be suitable for given climate conditions or would not be feasible due to high operational costs and energy requirements. Therefore, only those solutions that are potentially applicable at Kristineberg are described below. The solutions described are based on sulfide precipitation, coagulation, electrocoagulation, adsorption, and filtration.

**Sulfide precipitation**

As described in the Section 2.2.2 Sulfide precipitation, sulfide precipitation has significant advantages compared to neutralization. Mainly due to smaller volume of sludge produced and possibility to smelt it. Currently sulfide precipitation solutions are provided by such companies as BQE Water, Ion Exchange Company, and Paques.

BQE Water (BioteQ Environmental Technologies) has developed two sulphide precipitation process technologies for mine water treatment. ChemSulphide® utilizes sodium hydrosulphide (NaHS) for the removal of base metals, while BioSulphide® uses biologically generated hydrogen sulphide gas ($H_2S$). Generally, BioSulphide® is used for high metals loading and higher sulphide demand because it has lower operation cost per tonne of sulphide required [39]. Table 2 below shows operational parameters of ChemSulphide® plant built in Colorado:

*Table 2. Parameters of 34 $m^3/h$ ChemSulphide® plant at Wellington Oro mine* [39].

| Parameter | pH | Cadmium, mg/l | Zinc, mg/l |
|---|---|---|---|
| Feed | 6.2 | 0.12 | 1353 |
| Effluent target | 6.5-9.0 | 0.004 | 0.225 |
| Actual effluent | 6.65 to 7.00 | <0.0005 | <0.090 |

The plant produces less sludge compared to lime treatment, and all of it is shipped to smelters.

In China 1000 $m^3$/h ChemSulphide® plant was built, which consists of a ferric iron removal stage prior to the copper recovery stage. Ferric iron is removed to reduce NaHS consumption associated with ferric to ferrous iron reduction. Process flowsheet is shown in the Figure 2 below:

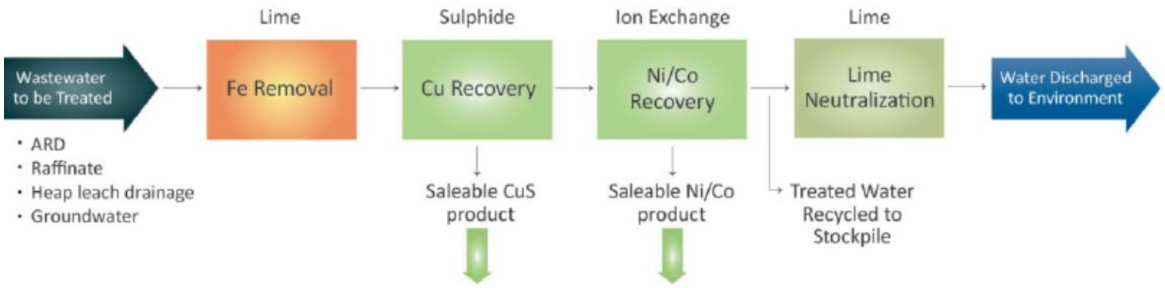


*Figure 2. Process flowsheet of ChemSulphide® treatment plant* [39].

Typical influent and effluent concentrations of the copper recovery plant are shown in the Table 3 below.

*Table 3. Parameters of 1000 $m^3$/h ChemSulphide® plant at Dexing Mine, China* [39].

| Parameter | pH | Copper, mg/l | Ferric iron, mg/l | Ferrous iron, mg/l |
|---|---|---|---|---|
| Feed chemistry | 2.2-2.6 | 149 | 909 | 386 |
| Copper effluent chemistry | 3.0 | <3 | 126 | 536 |

In 2003 ChemSulphide® plant was also installed at Raglan nickel mine in Canadian subarctic, and was able to treat on average 240 $m^3$/h of 4 to 40 mg/l Ni water to concentrations below 0.25 mg/l. The plant replaced a LDS lime plant and was successfully producing high-grade Ni concentrate, eliminating the need for sludge disposal [40].

As could be seen from the above, ChemSulphide® is capable of treating high volumes of water with high metal concentrations. The savings of lime reagent and possibility to sell sludge for profit make this technology attractive for investments. Reduced volumes of lime sludge is also an advantage.

Another sulfide treatment option is SULFATEQ™. It was developed by Paques for treating high sulfate content water (11 5000 – 25 000 mg/l) at wide pH range (2-8) to achieve less than 300 mg/l sulfate content in the effluent. The plant first converts sulfate into dissolved sulphide in a bioreactor, which utilizes alcohol or hydrogen gas as an energy source. Then in the oxidizing step by means of aeration sulphide is converted into hydrophilic (non-clogging) elemental sulphur, which could be then separated from the liquid phase. The produced sulphide could be used for recovery of valuable metals such as copper, nickel and zinc. The two-step process is depicted in the Figure 3 below [41]. In Finland and Sweden discharge limits for sulfates are currently enforced only for a few mines [38], but there is a trend in making sulfate removal obligatory. Therefore, this process could be of an interest, as it offers simultaneous metals and sulfate removal. However, currently there is a problem with operation of sulfate-reducing bioreactors in cold climate.

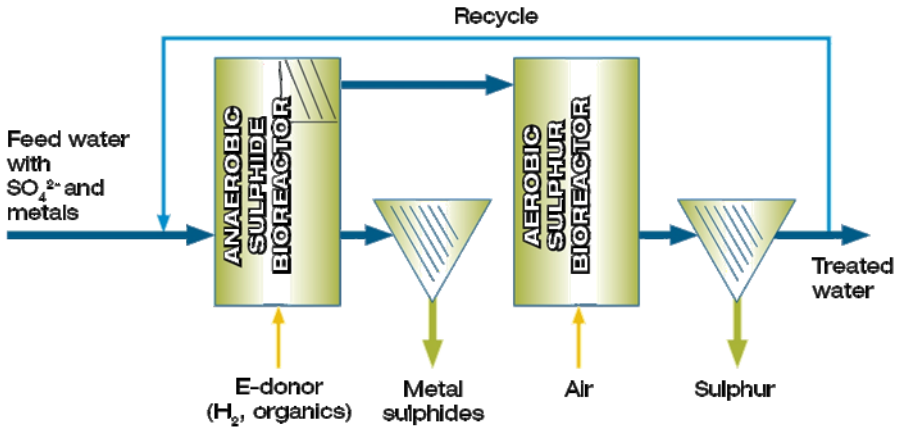


*Figure 3. Process flow scheme of SULFATEQ™ treatment plant [41].*

Another technology developed by Paques is THIOTEQ™. It was designed for removal of dissolved metals from water with initial concentrations from 50 to 5000 mg/l. The process consists of sulfate-reducing bioreactor that produces $H_2S$ gas from inexpensive sulphur source, while utilizing a carbon source (e.g. ethanol). Produced gas is then fed to a contactor, where it reacts with metals that form insoluble sulfides. The precipitate is then removed in a clarifier, and pH of water is adjusted with lime before discharge. One example of THIOTEQ™ installation is shown in the Figure 4 below. Produced water contains less than 0.01 mg/l copper [42]. The advantage of sulfate-reducing bioreactor compared to chemical sulfide dosage is lower cost per ton of metal sulfide produces. No storage and transportation of hazardous sulfide is required, as it is produced on-site and on-demand [43]. However, operation of bioreactor is complicated, as cultivation of bacteria takes time, and the colony could be sensitive to changes in environment, such as temperature. In Swedish climate operation of bioreactor is likely to be unreliable.

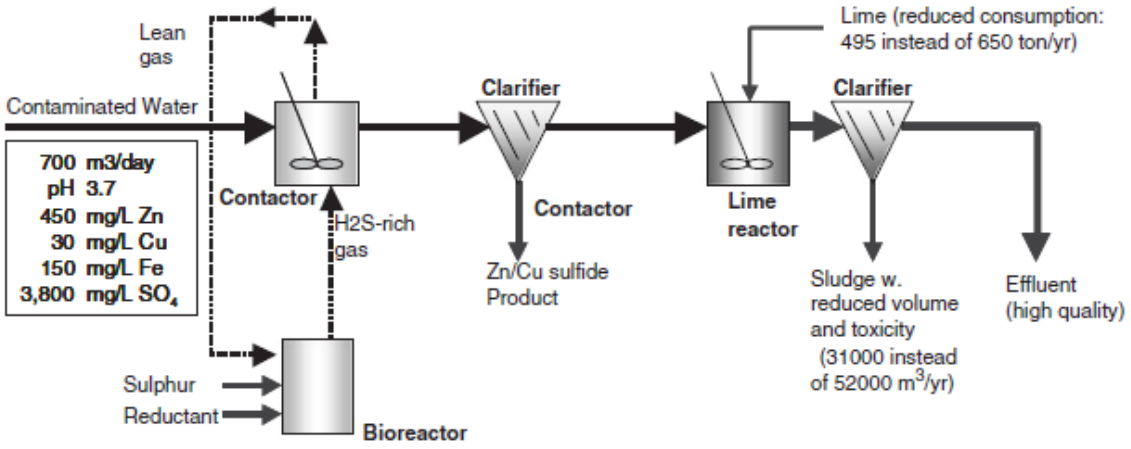


*Figure 4. Flowsheet of Paques THIOTEQ™Metal at North American zinc mine [42].*

**Coagulation**

Another option for chemical treatment of AMD is coagulation and flocculation, followed by clarification. These well-known treatment methods have been improved by Veolia, which offers Actiflo® process for removal of metals from water. Actiflo® is an extremely

compact clarifier, which uses microsand for improved floc formation and sludge settleability. Sand is separated from sludge in a hydrocyclone and returned back to the process, which saves costs [44]. Scheme of the process could be seen in the Figure 5 below:

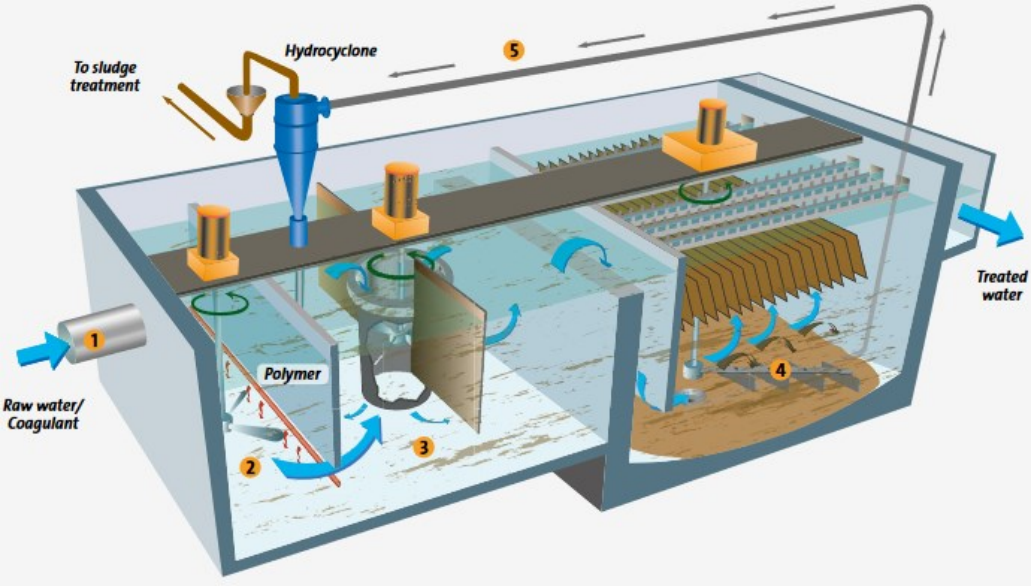


*Figure 5. Actiflo® clarifier produced by Veolia. 1 – chemicals addition, 2 – coagulation, 3 – Turbomix™ flocculation, 4 – clarification, 5 – recirculation* [44].

Actiflo® could be used as a polishing step after lime neutralization, or instead of thickener in a HDS process. The advantage of this equipment is compact design and very low residence time, which allows for rapid adjustments to the process depending on influent water volume and quality. Sludge volume is lower than in case of lime neutralization, though metals are precipitated as hydroxides. High cost of microsand is a drawback.

**Electrocoagulation**

Electrocoagulation is an emerging water treatment technology that is based on release of coagulating agents by electrodes submerged into water. Companies that offer electrocoagulation solutions include P2W, OWA of Owatec Group (in pilot testing now), Outotec, WaterTectonics, F&T Water Solutions, and Axolot.

P2W offers a patented electrocoagulation technology that was designed to treat large volumes (hundreds of $m^3$/h) of acid mine drainage. The electrocoagulation process consumes electrical energy and pure metal electrodes, which release coagulant to water (typically hydroxylated iron and aluminium [45]), therefore eliminating need for chemical reagent dosage. The average power consumption per cubic meter per hour is around 0.1-0.5 kWh and the period between the replacement of electrodes ranges between 6 and 12 months. This process is designed to precipitate metals as hydroxides [46]. The average treatment efficiencies are shown in the Table 4 below:

*Table 4. Key features of P2W's electrocoagulation technology* [46].

| Parameter | Cr | Cu | As | Ni | Zn | Al | Pb | Mn | Ca |
|---|---|---|---|---|---|---|---|---|---|
| Feed, mg/l | 125 | 200 | 529 | 26 | 250 | 130 | 35 | 40 | 520 |
| Effluent, mg/l | < 0.1 | < 0.1 | < 0.05 | < 0.1 | < 1 | < 1 | < 0.1 | < 0.1 | < 20 |

WaterTectonics has developed WaveIonics electrocoagulation enhanced filtration technology that could work with high flows (up to ca 220 $m^3$/h), in low temperatures and wide pH range. This technology was used for clean-up of tailings pond in Montana. Treatment consisted of electrocoagulation followed by RO filtration [47]. Operational parameters of the treatment plant are presented in the Table 5 below:

*Table 5. Water quality before and after WaveIonics treatment plant in Montana* [47].

| Parameter | Units | Influent | EC effluent | RO effluent |
|---|---|---|---|---|
| Total suspended solids | mg/l | 32 | 11 | 0.1 |
| Total dissolved solids | mg/l | 11700 | 11800 | 714 |
| Sulfate | mg/l | 4770 | 4480 | 34 |
| Iron, total | mg/l | 266 | 0.22 | 0.01 |
| Manganese, total | mg/l | 11.4 | 0.768 | 0.005 |
| Arsenic, total | mg/l | 3.21 | 0.01 | 0.003 |

The advantages of electrocoagulation over conventional coagulation process include absence of secondary contamination, low sludge volumes, and elimination of chemical reagents handling, as they are produced on-site. Electricity consumption could be a constraint. Moreover, not all contaminants could be removed simultaneously, so multi-step coagulation set-up may be required [45].

**Adsorption in fluidized bed columns**

Krüger A/S Denmark (owned by Veolia) has developed MetClean™ technology based on fluidized bed columns for heavy metals removal from water. MetClean™ unit consists of two fluidized bed columns filled with microsand. First column comprises iron process, and the second one manganese process. The columns could be used together as well as separately or in combination with other treatment units. In the iron process water enters the reactor from the bottom together with $FeSO_4$ and an oxidizing agent (e.g. NaClO). In the manganese process water is mixed with $MnSO_4$ and $KMnO_4$. Oxidized metals forms coating layers on the surface of microsand grains, and by adsorption pollutants are encapsulated in the layers of constantly forming adsorptive active surfaces. When granules become few times heavier than the original sand grain, they are removed [48]. The process does not have a sand recovery step, unlike Actiflo®. But the obtained sludge could be easily dewatered, and when dry it is easy to handle and transport. Overall, it has significantly better properties than conventional gypsum sludge.

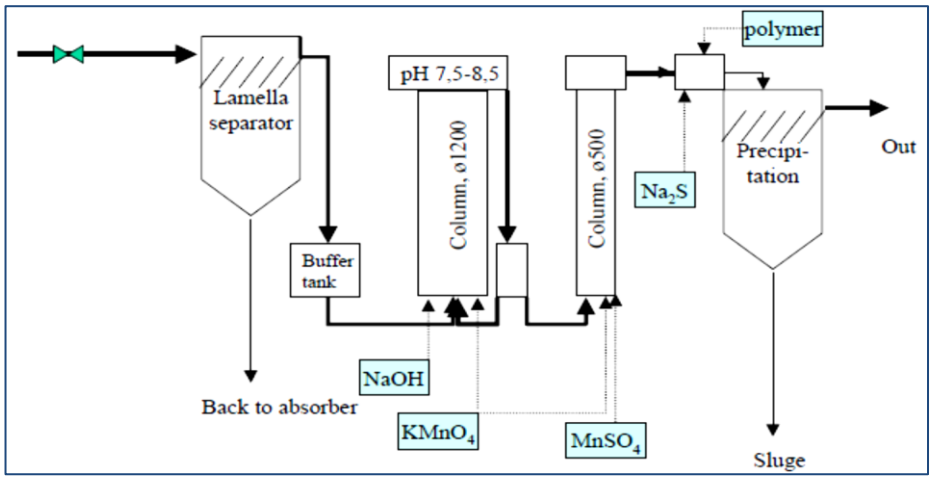


*Figure 6. Process scheme of full scale MetClean™ pilot plant in Avedøreværket for treatment of fluegas washwater* [48].

One example of MetClean™ application is removal of heavy metals from flue gas washwater (see Figure 6). A pilot plant was tested at Danish power plant Avedøreværket. Existing gypsum precipitation was supplemented by lamella clarifier, followed by two Mn process columns. The inlet water contained 20 to 70 mg/l Mn(II), which was utilized in the process. The first column was able to remove all Mn(II) and most of the heavy metals (mainly Cd, Ni, Zn, and also Co, Cu, As, Cr, Pb). The second column served as a polishing step and had no recirculation. Tests were also made to supplement the MetClean™ process with post-precipitation using sulfide, and the results could be seen in the Table 6 below. The inlet flow was 5 $m^3$/h and recirculation flow to the first column 25 $m^3$/h.

As could be seen from the Table 6 below, even after sulfide post-precipitation effluent concentrations of most of the metals were higher than 1 µg/l, and almost no zinc was removed during sulfide precipitation. These was the best reference result found during the literature review, and it shows that removal of metals below values proposed in the present thesis is extremely hard to achieve.

*Table 6. Kristineberg inlet water quality and results from 5 $m^3$/h pilot tests of MetClean™ with sulfide post-precipitation for treatment of flue gas wash-water at Avedøreværket, unfiltered samples* [48].

| Unfiltered sample | Units | Kristineberg inlet for comparison | Column 1 inlet (after neutralization) | Column 1 effluent | Column 2 effluent | Post-precip. effluent |
|---|---|---|---|---|---|---|
| Ba | µg/l | 43 | 1150 | 463 | 405 | 334 |
| Cd | µg/l | 191 | 91 | 13 | 20 | 3.7 |
| Co | µg/l | 311 | 219 | 11.1 | 18 | 3.9 |
| Cr | µg/l | 40 | 6.6 | 5.5 | 5.5 | 2.6 |
| Cu | µg/l | 23400 | 15 | 18 | 11 | 2.3 |
| Hg | µg/l | 0.09 | 0.1 | 0.1 | 0.04 | 0.03 |
| Ni | µg/l | 95 | 387 | 14,8 | 29.1 | 6.8 |
| Pb | µg/l | 89 | 8.8 | 2.8 | 2.8 | <0.6 |
| Se | µg/l | na | 132 | 7.2 | 61.9 | na |
| Zn | µg/l | 81600 | 1830 | 92 | 125 | 105 |

**Filtration**

There is also a number of companied that provide membrane filtration solutions, for example Veolia, Liqtech, Lenntech, Cembrane, Porex Filtration, and Bauer Water GmbH.

Porex Filtration division offers POREX® Tubular Membrane Filter™ modules for metal contaminated wastewater treatment and reclamation (Figure 7). They claim to reach levels of less than 1 ppm suspended solids and less than 0.1 ppm metals in the effluent [49]. However, chemical pre-treatment is required for pH adjustment, oxidation/reduction depending on metals present, as well as coagulant feeding. Membranes also have to be chemically cleaned to avoid fouling.

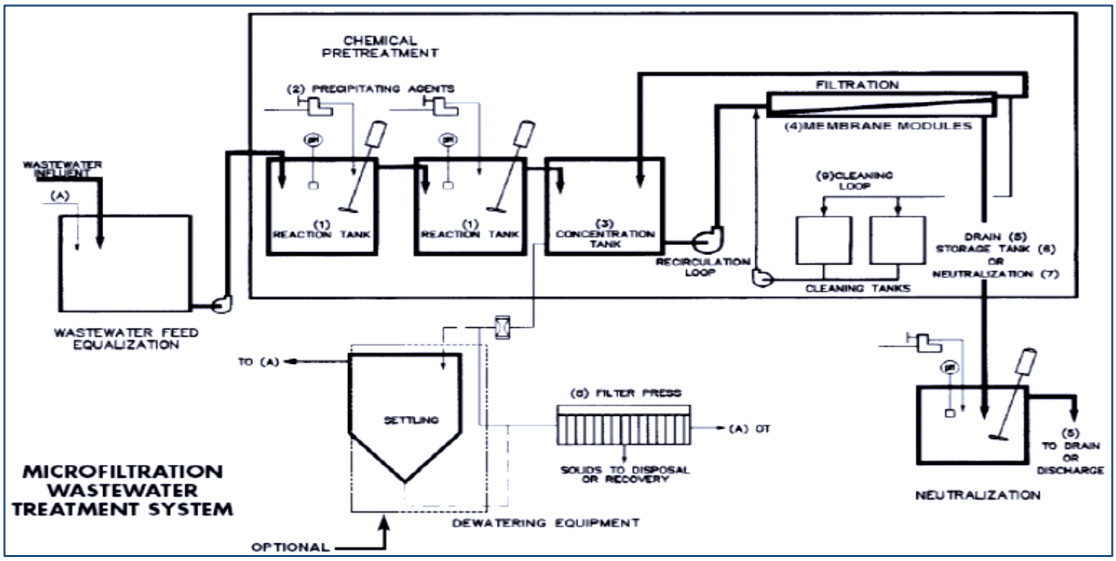


*Figure 7. Treatment process scheme of Porex Tubular Membrane Filter Modules in combination with chemical precipitation* [49].

The disadvantage of membrane filtration for AMD treatment includes high capital and operational costs, high energy requirements, problems with clogging, fouling, and leaking of membranes. They also have limited lifetime of about 5-10 years. The necessity to chemically clean or backwash filters means that extra capacity is required to cover for downtime during washing. Moreover, produced concentrate is typically not usable and requires further treatment before disposal. These makes membrane filtration solutions unattractive as a main stage of AMD treatment, but they could be used as a polishing step for removal of residual suspended matter from water.

**Summary**

As could be seen from all of the above, often several solutions are combined in order to achieve high treatment efficiency. However, none of the solutions described in this Section seem to reach effluent quality targets that should be achieved in the present thesis work. On average they seem to reduce individual metal concentrations to a level between 1 mg/l and 0.1 mg/l, but not below 1 µg/l. The most attractive technology seems to be chemical sulfide precipitation of metals, as it could work in cold climate and allows production of sellable product. Selling the obtained sludge to smelters could cover the operational costs of treatment plant and decrease sludge disposal expenses.

# 3 Site description and data

Kristineberg is an underground Cu-Zn mine located in the Västerbotten region in northern Sweden. Since discovery of the ore body in 1918 there have been ten mines operating within 50 km distance from Kristineberg, but currently it is the only remaining active mine [50]. Kristineberg mine produces ores containing mostly Cu and Zn, but also Pb, Ag, and Au [51]. The mine has such sulfide-bearing ore minerals as pyrite ($FeS_2$), chalcopyrite ($CuFeS_2$), sphalerite (ZnS), and galena (PbS) [52]. Sulfide oxidation of pyrite-rich Zn-Cu ore is the primary case of AMD formation at Kristineberg.

Boliden is continuously engaged in exploration of new resources, and exploration works in the area showed that the ore body continues in the direction of Rävliden, approximately 2.5 km west of the Kristineberg ore deposit [3]. This deposit is an important part of the Boliden area's continuous development. However, expansion of the mine will result in increased volumes of AMD that require treatment.

## *3.1 Kristineberg water treatment plant*

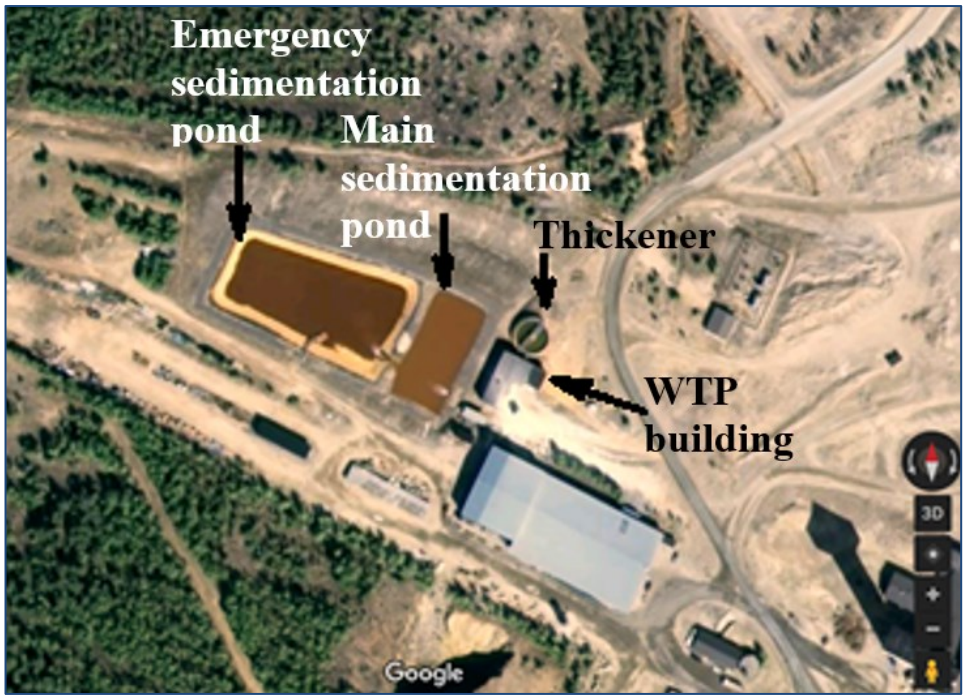


*Figure 8. Kristineberg water treatment plant, view from above (Google maps).*

Top view of Kristineberg water treatment plant is shown on the Figure 8 above. Total amount of water collected from the mine area is on average 100 $m^3/h$, which is a maximum capacity of the treatment plant. Due to the capacity limit sometimes part of the water is diverted from the treatment plant and treated only with lime addition followed by sedimentation in the tailings pond. This happens when amount of collected mine water increases or if there are disturbances in plant's operation.

Table 7 below shows average influent water quality at Kristineberg during the period from January 2014 until July 2017. It can be seen that the AMD contains a vast number of toxic contaminants at high concentrations and requires treatment.

*Table 7. Kristineberg average influent composition during the period from 01.2014 to 07.2017, assuming inflow rate of 100 $m^3/h$.*

| Parameter | Concentration, µg/l | Potential recovery, kg/d | Parameter | Concentration, µg/l | Potential recovery, kg/d |
|---|---|---|---|---|---|
| Al | 73993.0 | 177.6 | Mn | 3950.7 | 9.5 |
| As | 38.1 | 0.1 | Na | 60411.6 | 145.0 |
| Ba | 29.0 | 0.1 | Ni | 76.3 | 0.2 |
| Ca | 339209.0 | 814.1 | Pb | 104.4 | 0.3 |
| Cd | 185.9 | 0.4 | S | 855767.0 | 2053.8 |
| Co | 266.6 | 0.6 | Sb | 1.8 | 0.0 |
| Cr | 40.7 | 0.1 | Si | 17543.3 | 42.1 |
| Cu | 17380.7 | 41.7 | Sr | 1118.1 | 2.7 |
| Fe | 166142.0 | 398.7 | U | 25.8 | 0.1 |
| Hg | 0.0 | 0.0 | V | 1.8 | 0.0 |
| K | 33332.6 | 80.0 | Zn | 79644.2 | 191.1 |
| Mg | 147047.0 | 352.9 | TOTAL SUM, mg/l | 1796.3 | 4311.1 |

Based on the data presented above average weight-% of the most important contaminants in the water was calculated. Iron accounts for 9.25% of the TDS, while Zn, Al, and Cu account for 4.43%, 4.12%, and 0.97% respectively. In the end of 2017 approximate prices for metals were 3577 USD/t for Zn and 7066 USD/t for Cu [53]. Assuming same mass flow of metals in 2017 as during this period, and 65% profit from recovery, cost of Zn and Cu that were lost at the treatment plant in 2017 is approximately $210600 and $91000, respectively.

Based on the data from water quality monitoring program ionic balance of water was calculated. It showed that average concentration of anions through the monitoring years was 49.86 mEq/l and that of cations 49.64 mEq/l. The error could be attributed to the varying concentrations and the fact that metals are present in water in different valence forms that were not accounted for in the calculation. Average conductivity of water was 3361 µS/cm and average concentration of TDS was 1796 mg/l. Ratio between calculated average TDS and measured average conductivity is 0.53, which correlates well with the literature values of 0.4-0.8.

Current scheme of the water treatment process at Kristineberg is shown in the Figure 9 below. Water collected from the mine area is first settling in two sedimentation ponds, which are designed to decrease suspended solids load on the plant. Mine water is pumped to the main pond, which has a volume of 2000 $m^3$, while the second emergency pond with volume 8000 $m^3$ serves as a water storage during extreme events or when plant is not in operation. Water is recirculating from emergency to the main pond to avoid freezing during winter and to equalize water quality.

The water treatment process is based on High Density Sludge system (HDS) and consist of two stages, namely pH adjustment and thickening. For pH adjustment slaked lime is used, which is produced on-site. Adjustment of pH after pre-sedimentation is done in 3 mixing tanks. In the first tank (V = 50 $m^3$) acidic water is mixed with recirculated sludge

from the thickener to reach pH 7.5. Recirculated sludge is added to tanks 1 and 2 through a split box in portions that depend on pH in tank 1 and/or total sludge recycling rate. Recirculated sludge creates crystallization centres and helps to improve formation of flocs and their settleability. Moreover, it aids to decrease lime consumption. Typically recirculation is ca 15% of incoming water volume.

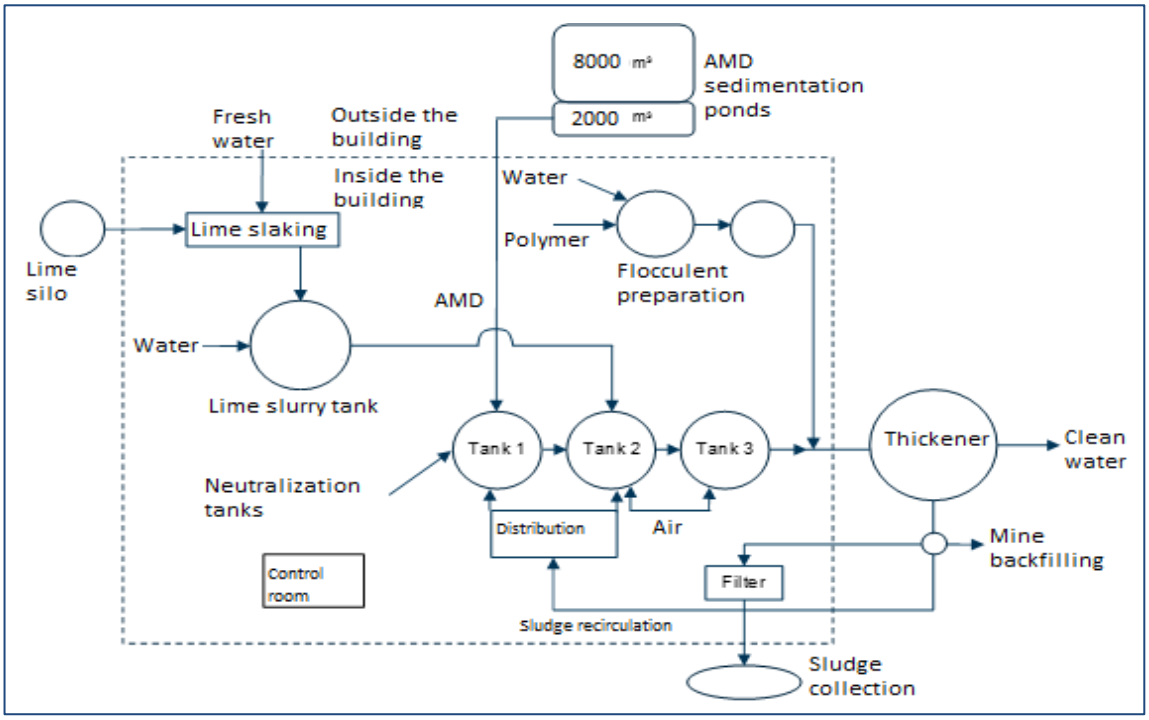


*Figure 9. Scheme of water treatment at Kristineberg* [54].

In the second tank (V = 62 $m^3$) lime is added to further increase pH to 9.5. The second and third tanks were designed to be aerated, but this option is currently not used, because most of the iron in feed water is in ferric form. Diluted polymer Magnafloc® 10 (BASF Mining Solutions) is added to the inflow of the third tank (V = 62 $m^3$), where big flocs are formed. Polymer is diluted on-site to obtain 0.05% solution. From the third tank water flows to the radial thickener (V = 770 $m^3$, D = 14 m, with inflow of 100 $m^3$/h surface load is 0.65 m/h). Part of the sludge is then recirculated back to the first and second tank, and part is led to a dewatering stage, which consists of a drum filter. After thickener sludge contains about 30% solids, and after drum filter solids content increases to about 60% [55]. Sometimes underflow from clarifier is used for mine backfilling without prior dewatering.

Initially thickener was dimensioned for a pilot plant to treat 20 $m^3$/h AMD with a safety factor of 2. Later during the design it was considered that AMD flow could be as high as 70 $m^3$/h and have more diluted concentrations, so all equipment was scaled up except the thickener, which was built with diameter of 14 $m^2$, because thickener cost is a large portion of total project cost [55]. Since the start-up plant's inflow has been ca 100 $m^3$/h. Previously presence of turbulence in the clarifier was reported, which could be a factor affecting effluent suspended solids. It was also reported that keeping sludge in the thickener for more than one day is beneficial for crystals growth and sludge maturing, which improves further filtering. However, sludge should not take most of the thickener volume,

otherwise suspended particles would not have enough time to settle and would end up in the effluent.

Drum filter decreases volume of the sludge, however, dewatered sludge still has high water content, is very sticky, and hence is difficult to transport. So currently it is more preferable to pump underflow from the thickener, mix with sand, and dispose as a back-filling material for the mine. But since backfilling is presently required only about once in two weeks, other means of sludge storage and disposal have to be utilized.

Treated water from the thicker and drum filter flows via a creek and impoundment 3 to a lime station at the beginning of impoundment 4, where it is mixed with flows of mine drainage from abandoned mines in the area. There lime is added as a final treatment step to ensure metals removal. Sludge formed after lime addition settles in impoundment 4 before water is discharged to the recipient [54].

For lime slaking quicklime is supplied from a silo to a mixing tank, to which clean water is added. Temperature increases to about 52 °C due to exothermic reaction of lime slaking. Then the suspension is pumped to a buffer tank, where it should be diluted with clean water to bring the temperature down. The problem was that both water flows were coming into the mixing tank, so quicklime/water ratio was too low, resulting in low temperature. Before this thesis was completed the second flow was diverted to the buffer tank, and temperature of lime slaking increased to 63 °C. Reaching the optimum temperature of 70 °C by adjusting quicklime and water flows would help to improve efficiency of lime consumption and metals removal rate.

## 3.2 Kristineberg tailings pond

Currently there are five tailings impoundments in the Kristineberg area that are used to treat tailings and AMD (Figure 10). There used to be a concentrator near the mine, but it was moved, so now no tailings are produced in the area.

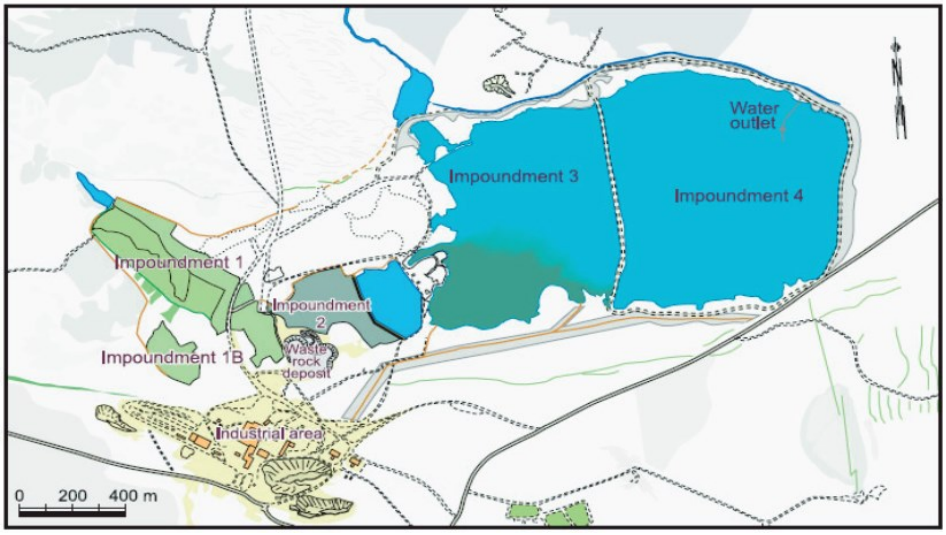


*Figure 10. Map of the Kristineberg mine area with impoundments 1, 1B, 2, 3, and 4 of the tailings pond* [51].

Impoundments 1, 1B, and 2 have been partially remediated and are not in use anymore. Impoundment 3 is currently partly covered with till. Before entering the impoundment 4 effluent from the treatment plant mixes with runoff from the area and passes a liming station, which is the last stage of water treatment prior to its discharge into a small river Vormbäcken. Through Vormbäcken water flows about 40 km in south-east direction via Lake Vormträsket into River Vindelälven. The catchment is a heavily protected area, as Vindelälven is one of four rivers in northern Sweden not obstructed by hydropower plants and therefore considered a pristine environment. One of the most important species inhabiting the river is naturally reproducing salmon. According to a Swedish national law NRL the surrounding creeks contributing with water to the main river are protected as well as the river [56]. Vindeläven belongs to Natura 2000 network of protected areas of the EU. However, the background metal concentration levels in Vormbäcken are elevated due to presence of abandoned mines Hornträskgruvan and Rävlidmyrgruvan upstream from the impoundment 4 discharge point. The mixing ratio between Vormbäcken water and discharge from impoundment 4 is 12:1 during high flow events (snowmelt in May) and 3:1 during low flow periods. The catchment area of the tailings pond is smaller than that of the river upstream. Currently, during normal operation discharge water actually dilutes water in Vormbäcken in terms of Cd, Cu, and Zn concentrations. Discharge water has high ionic strength and Ca concentrations, which causes flocculation of dissolved organic matter and association of trace metals in particles. Calcium present in discharged water is thought to reduce toxicity of metals in Vormbäcken water and decrease the distance of their transport [52]. According to Water Information System Sweden Vormbäcken is classified as surface water body with bad ecological and chemical status [57].

Since 2012 Boliden Mineral AB runs a monitoring program that includes monthly sampling and analysing of water upstream from the discharge point, in the discharge point, and downstream from it. Water discharged from the tailings pond is monitored weekly and also as monthly average (at least to individual measurements). Samples are sent to ALS laboratory for determination of total metal concentrations (suspended and dissolved), phosphate, and also nitrogen species. Monitoring shows that in the sampling points metal concentrations have been continuously decreasing since the monthly monitoring program has started.

## 3.3 Proposed discharge requirements and current water treatment efficiency

Based on the requirements of EU WFD and obligation to achieve at least good quality ecological status for surface water bodies, Boliden Mineral AB has prepared a proposal for environmental discharge limits for the extension of Kristineberg mine (see Table 8 below). The basis for these requirements is Marine and Water Authority Regulations (HVMFS 2013:19) on classification and environmental quality standards for surface water [58]. Detailed instructions and descriptions of how these regulations should be applied on practice are given in [59]. The maximum allowed monthly average concentration is calculated from at least two individual measurements. Maximum allowed concentration is a concentration that should not be exceeded at an individual measure [58]. Based on these regulations Boliden Mineral AB created a proposal for environmental requirements that could be imposed on Kristineberg mine in the future. As could be seen from the Table 8 below, proposed limits are much stricter than those that are currently being used.

These limits are related to water discharged to the recipient, and not effluent from the treatment plant. But for simplicity hereafter it is assumed that this are treated water requirements.

*Table 8. Kristineberg incoming water parameters for the year 2016, the proposed environmental permit requirements, and current requirements.*

| Parameter (unfiltered sample) | Incoming water, µg/l | Proposed requirements | | Current requirements | |
|---|---|---|---|---|---|
| | | Monthly average, µg/l | Maximum allowed, µg/l | Monthly average, µg/l | Maximum allowed, µg/l |
| Al | 69350 | | | | |
| As | 35 | 0.5 | 8 | 5 | 10 (2 months) |
| Cd | 173 | 0.25 | 1.5 | 2 | 4 (2 months) |
| Cr | 31 | 3.4 | | - | |
| Cu | 15381 | 0.5 | | 15 | 30 (2 months) |
| Fe | 147433 | | | | |
| Hg | 0.03 | | 0.07 | - | |
| Ni | 72 | 4 | 34 | 5 | 10 (2 months) |
| Pb | 82 | 1.2 | 14 | 5 | |
| U | 18 | | 8.6 | - | |
| Zn | 74283 | 6 | | 300 | 600 (2 months) |
| Suspended material | | | | 10 mg/l | |
| pH | 3 | | | ≤7 pH ≤10 | |

Samples of mine water incoming to treatment plant are taken once a month at different days and sent to ALS laboratory for total concentration analysis. Samples of outflowing water from the treatment plant are also taken once a month for analysis of total concentrations, nitrogen and phosphorus species (N-tot, $NH_4$, $NO_2$, $NO_3$, P-TOT, $PO_4$-P), suspended solids, and oil concentration. Nitrogen is not analysed in incoming mine water due to assumption that no nitrogen is removed from water by the treatment process, i.e. influent and effluent concentrations are equal. This assumption was supported by nitrogen species analysis of water sample used for this thesis work made by ALS and its comparison to the effluent water quality data.

The water quality parameters before and after the treatment at the Kristineberg WTP are presented in the Table 9 below.

*Table 9. Incoming and treated water quality at the Kristineberg WTP based on average monthly values from 2016.*

| Parameter (unfiltered sample) | Unit | Incoming water | Treated water | Removal % |
|---|---|---|---|---|
| Al | µg/l | 69350 | 684 | 99.01 |
| As | µg/l | 34.9 | 1.3 | 96.27 |
| Ba | µg/l | 30.9 | 28.5 | 7.71 |
| Ca | mg/l | 345 | 769 | na |
| Cd | µg/l | 173 | 2.3 | 98.66 |
| Co | µg/l | 250 | 1.2 | 99.51 |
| Cr | µg/l | 31 | 0.5 | 98.38 |

| Parameter (unfiltered sample) | Unit | Incoming water | Treated water | Removal % |
|---|---|---|---|---|
| Cu | µg/l | 15381 | 36.4 | 99.76 |
| Fe | µg/l | 147433 | 248 | 99.83 |
| Hg | µg/l | 0.03 | 0.01 | 62.03 |
| K | mg/l | 36 | 37 | na |
| Mg | mg/l | 148 | 83 | 43.91 |
| Mn | µg/l | 3935 | 268 | 93.19 |
| Na | mg/l | 67 | 68 | na |
| Ni | µg/l | 72 | 0.4 | 99.47 |
| Pb | µg/l | 82 | 11.8 | 85.64 |
| S | mg/l | 852 | 823 | 3.34 |
| Sb | µg/l | 1.5 | 0.1 | 93.62 |
| Si | µg/l | 16558 | 478 | 97.11 |
| Sr | µg/l | 1213 | 1390 | na |
| U | µg/l | 18.2 | 0.2 | 99.13 |
| V | µg/l | 1.3 | 0.1 | 92.14 |
| Zn | µg/l | 74283 | 191 | 99.74 |
| Conductivity | µS/cm | 3567 | 3347 | |
| $SO_4$ | mg/l | 2390 | 2289 | 4.22 |

From the data above it could be seen that most of the metals are removed with over 90% efficiency. Increase in calcium concentration is due to the lime addition, which also explains slight increase of sodium, potassium, and some other element concentrations. However, these removal rates are not sufficient to comply with the new discharge requirements shown in the Table 8.

From all mentioned above it could be concluded that there are two issues that have to be addressed in order to meet the proposed limits. First, for the existing treatment plant to meet these requirements its operation has to be optimized and a polishing treatment step should be added. Second, if the mine is expanded a new treatment plant would be required. Then new technologies could be used to achieve better metals removal and decrease amount of sludge produced. The experimental part of this work described below examines potential solutions for polishing treatment and construction of a new plant.

# 4 Materials and methods

Materials and equipment for conducting experimental work were provided by the laboratory of Boliden Mineral AB. Acid mine drainage was taken from the inlet to the Kristineberg's first sedimentation pond prior to the treatment plant on 12.09.2017 and 30.11.2017. Sampled water was sent to ALS Scandinavia laboratory for analysis (see Appendix 4). Reagents used in the screening experiments were industrial grade, and for the main experiments analytical grade reagents were used. List of all reagents used in this thesis is presented in the Appendix 8.

**Analytical procedures**

During preliminary tests equipment available in laboratory of Boliden Mineral AB was used. Samples from the main tests were sent to ALS Scandinavia laboratory.

Temperature, electrical conductivity, and pH of water were measured using either Mettler Toledo or WTW pH 3210 meter. For rapid estimation of metal concentrations in liquid samples and sludge X-ray analyser Xepos was used. It provided reliable results for liquid samples with high metals concentration and sludge samples, but measuring concentration in range of 1 μg/l was not possible.

During preliminary experiments total Fe and Fe(III) were analysed by quantitative colorimetric measurement of red-coloured ferric iron complex with 5-sulfosalicylic acid (SSA) followed by addition of ammonia and measurement of yellow-coloured complex of SSA with total iron [60]. This is a sensitive method that works when concentration of total iron in the solution is below 10 mg/l.

Attempts were made to analyse concentrations of seven dissolved metals (Al, Cd, Cr, Cu, Ni, Pb, and Zn) in liquid samples using Hatch Lange express analysis kits and spectrophotometers Hatch DR5000 and DR2800. These kits could be used for determination of trace concentrations of each metal according to instructions provided by the manufacturer. However, the procedure proved to be time-consuming and results were unreliable due to interference of other species. Analysis for Zn and Al was quite accurate compared to ICP analysis. Analysis of Ni, Cr, Cd, and Pb was not possible due to initially low concentrations of these elements in AMD. One major difficulty when using Hatch kits is that they are designed to be used in a narrow concentration range, but it is hard to predict sample dilution rate to obtain results.

Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES) Agilent 5510 VDV (Vertical Dual View) was used for determining concentrations of each element in liquid samples from screening tests. Radial view of plasma was used for the analysis. Diluted standard solution was prepared for plotting calibration curves. Sample preparation included filtering liquid samples through 0.45 μm filter to remove suspended particles and addition of nitric acid. Addition of 1 ml 25% acid to 5 ml sample helped to dissolve all the remaining suspended matter. Deionised water that served as blank was produced with ion-exchange filter containing Silex I B resin supplied by Silhorko-Eurowater A/S. The claimed conductivity of water after ion-exchange treatment is below 0.5 μS/cm [61], which should be equal about 0.2 mg/l dissolved matter.

# 5 Experimental part

The experimental part of this thesis consisted of four main parts. Firstly, AMD titration tests were conducted to estimate pH levels at which metals would precipitate as hydroxides and amount of alkali required to increase pH of Kristineberg AMD. Secondly, simulations were done in SolGasWater software to analyse solubility of metals in Kristineberg AMD during hydroxide and sulfide precipitation. Thirdly, several series of screening tests were done to test different treatment methods and different reagents to get an insight into water chemistry and processes that determine metals removal from mine drainage. Lastly, three series of main experiments were conducted in order to determine possibility to reach the proposed environmental limits.

## *5.1 Acid mine drainage titration*

To estimate pH levels for precipitation of metals and metalloids from the solution four titration test were conducted. Titrations were done with 0.1M NaOH solution prepared by dilution of solid NaOH pellets in tap water. AMD sample was poured from well-shaked canister into a beaker and placed on magnetic stirring plate. Sodium hydroxide was manually dosed from a burette. To continuously monitor pH a silver chloride pH electrode (Mettler Tolledo) was used. Titrations 1 and 2 were done with 100 ml samples, and titrations 3 and 4 with 200 ml samples. First titration was continued until pH 10.0, second until pH 9.9, third until pH 9.0, and fourth until pH 12.2.

During titrations 3 and 4 samples were taken from the solution to determine changes in metal concentration with pH increase. In the third titration samples were poured into vials and centrifuged to separate suspended solids. Clear solution was then analysed using Xepos, and then both suspended solids and liquid were returned to the sample and titration continued. Due to low accuracy of Xepos for determination concentrations in liquid samples the results of these analyses were not included in the present work. During titration 4 samples were taken from the solution with syringe and then filtered through 0.45 µm membrane to remove suspended solids. The removed volume was not accounted for when plotting titration curve, as it was assumed to be negligible compared to total volume of the solution. Iron content was analysed by spectrophotometer with SSA solution, while Zn and Al were analysed with Hatch kits. Hatch kits only determine metal concentrations within a certain narrow range, and it was rather difficult to predict required dilution rate for Zn and Al analysis. Due to errors attributed to high dilution rates the results of these analyses were not included in the present work but are discusses below.

Titration tests allowed to determine optimum pH levels for precipitation of metals from the solution. Titration curves shown in the Figure 11 below illustrate dependency of pH on the amount of 0.1 M NaOH solution dosed. Not all the results of titration 4 are presented, as it was continued until pH 12.2. It can be seen from the plots below that the titration tests had good repeatability.

From this titration curve equivalent acidity of $H_2SO_4$ could be calculated. The equivalence point is taken to be pH 7, at which point 18.5 ml of 0.1 M NaOH per 100 ml AMD were consumed, meaning 1.85 moles of NaOH were added to the 100 ml sample. Therefore, equivalent molarity of $H_2SO_4$ is 9.25 mM.

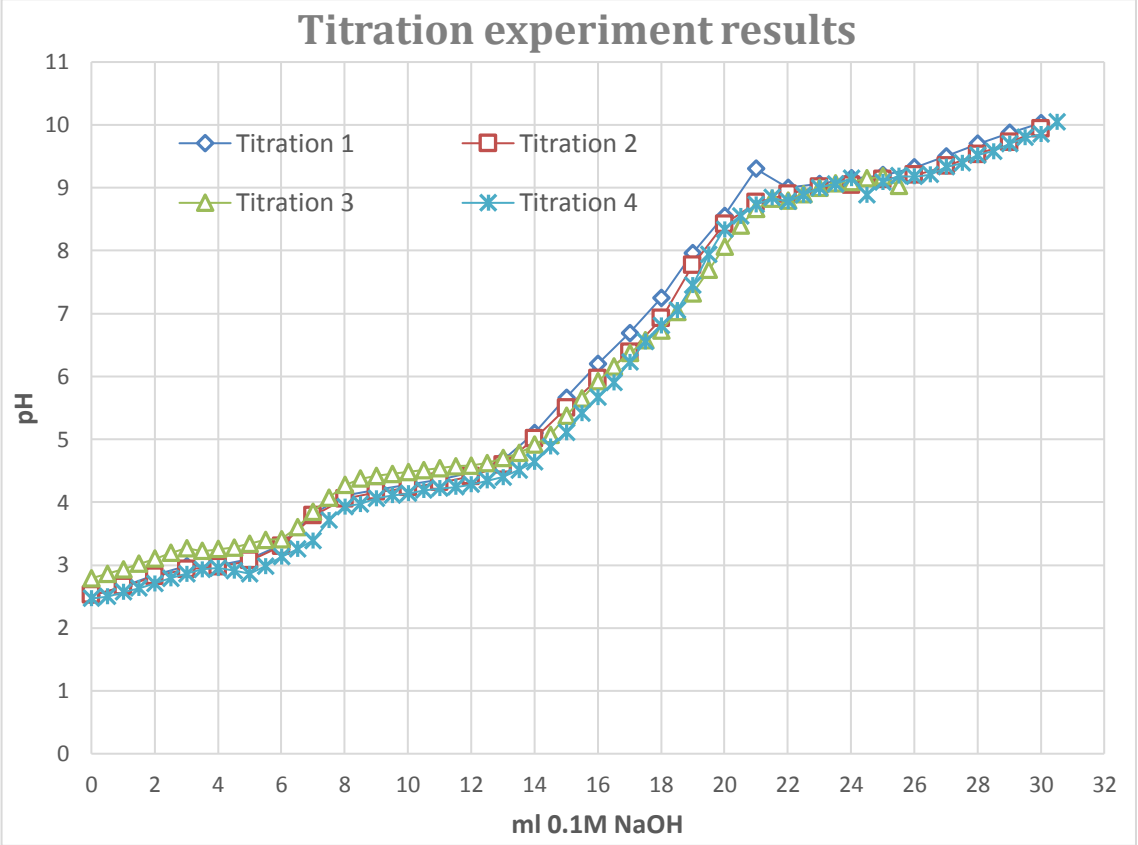


*Figure 11. Results of four titration experiments with 0.1M NaOH.*

During titration 4 analysis of Fe(III) and total Fe showed that at pH>3 there is no dissolved iron present in water, as it all precipitates as $Fe(OH)_3$, meaning that almost all iron in the solution is in its oxidized form Fe(III). Analysis of Al showed that its concentration decreased steadily and reached minimum at pH ca 6. However, it is important to remember that at pH over 10 aluminium hydroxide dissolves again.

This data correlates with the trends shown on the titration curve above. At pH 3 ferric iron consumes hydroxide ions and precipitates as $Fe(OH)_3$, therefore preventing pH from increasing while NaOH is added. After all iron precipitates, pH starts to increase again until it reaches pH 4.3, when Al starts to precipitate as $Al(OH)_3$. Then pH continues to increase slowly to 9 and then starts to buffer, presumably due to carbonate equilibrium and $CO_2$ gas adsorption.

## 5.2 SolGasWater modelling

SolGasWater (SGW) software was used to model solubility of metals in the Kristineberg water sample. The software was developed by Gunnar Eriksson at Umeå University for computation of chemical equilibrium systems. The program requires an input of components and all chemical species formed from them, as well as equilibrium constant (stability constant) for each species. User should also state whether species are in solid or aqueous state. When matrix of components and their species is created user can set up such parameters of the system as temperature, pressure, redox potential, and ionic strength of solution. The program then performs mass balance and thermodynamic calculations and solves them with free-energy minimization method. The output of calculations contains

data matrix with information about equilibrium composition of the system, which could be displayed in different forms according to the needs of the user [62].

### 5.2.1 SolGasWater hydroxide consumption model

There are several factors that affect solubility of metals in the AMD. These include temperature, ionic strength of the solution, formation of complexes and solids, alkalinity, presence of buffers and chelating agents, adsorption, co-precipitation, and aging of solid precipitate [63], [64], [65]. These factors make it difficult to build accurate models of metal ions behaviour in water. However, theoretical models and thermodynamic calculations can serve as a guide for organization of experiments and help to determine the general trends in solution behaviour.

For modelling hydroxide precipitation of metals the input concentrations of species were taken from the ALS laboratory analysis results of the Kristineberg AMD sample (Appendix 4, screening tests water analysis). Stability constants were taken from two sources [66], [67]. The input temperature was 25 °C, pressure 1 atm, redox potential 500 mV, ionic strength of solution 1M, and pH variation step of 0.1 pH unit. The output data provided numerous possibilities for analysing the AMD water chemistry, as it allowed understanding water composition at different pH levels and gave an insight into solubility of different species.

Figure 12 below shows the theoretical $OH^-$ ion consumption curve versus the titration curve average across the four experiments described earlier. The theoretical $OH^-$ consumption curve is divided into differently coloured regions based on consumption of hydroxide ion by different metals. These regions represent pH buffering of the solution due precipitation of metal hydroxides. Point where the colour changes represents start of precipitation of another metal hydroxide.

Precipitation regions of iron and aluminium can be clearly seen on the experimental titration curve, while it does not give a clear view of pH regions for precipitation of other metals. Hydroxide consumption by $Fe^{3+}$ matched the theoretical consumption curve almost exactly. It also corresponded to the literature data, which suggests that $Fe^{3+}$ precipitates at pH 3.0-3.5 as schwertmannite, which is brown-yellow amorphous Fe-oxyhydroxy sulfate mineral. It was found that schwertmannite at Kristineberg has formula $Fe_8O_8(OH)_{5.02}(SO_4)_{1.49}\bullet 0.5H_2O$ [21]. At pH above 4 iron could also precipitate as ferrihydrite (e.g. $(Fe^{3+})_2O_3\bullet 0.5H_2O$) [19]. Aluminium precipitation was observed at pH around 4.2-4.7. It also correlates with the literature on precipitation of aluminium as hydrobasaluminite (chemical formula $Al_4(SO_4)(OH)_{10}\bullet 15H_2O$)) [20], [63]. However, it could be seen that pH increase was slower compared to theoretical, which could be attributed to the kinetics of the reaction and slow release of sulfate ions from aluminium sulfate complexes. After Al had precipitated pH was rising steadily until 8.8, after which the increase slowed down, possibly due to $CO_2$ adsorption from the air.

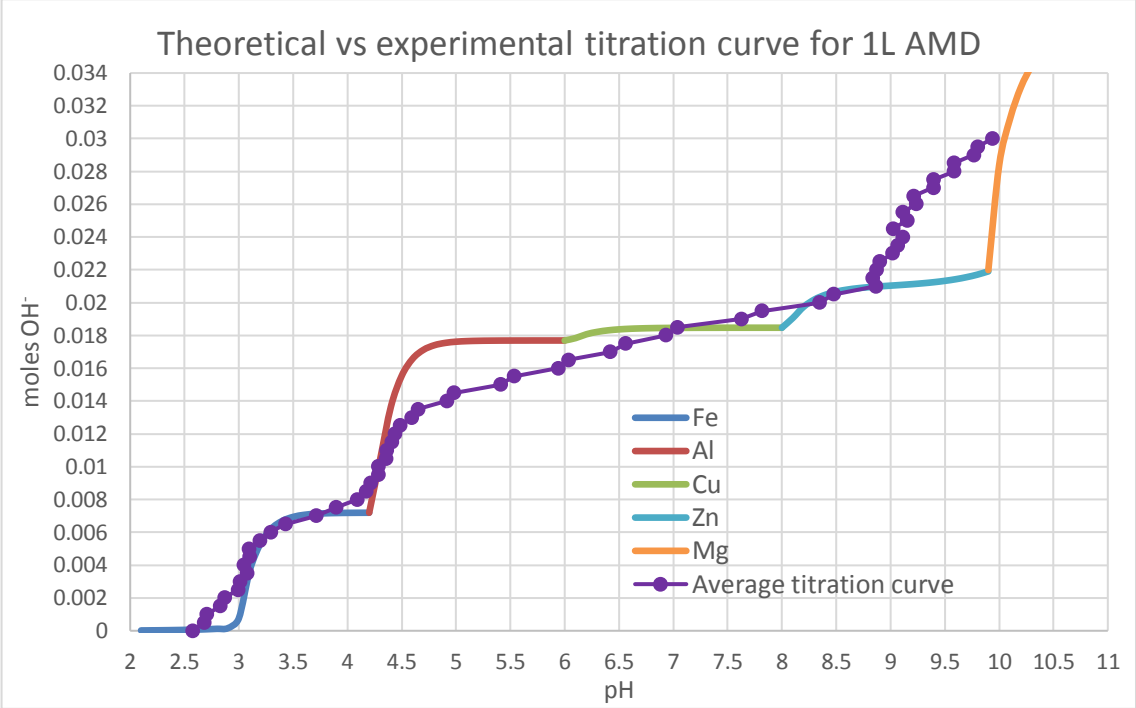


*Figure 12. Theoretical and experimental hydroxide consumption curves.*

As it can be clearly seen from the Figure 12 above, the total hydroxide consumption to achieve pH 10 is approximately same in both cases, which signifies good model validity. However, certain regions of the experimental curve differ considerably from the theoretical ones. It can be explained by the inaccuracy of the manual titration method and pH meter error, and the fact that theoretical curve represents the system in equilibrium, while the experiment system was not in equilibrium condition. Certain reactions take considerable amount of time to reach equilibrium state, but SGW does not take into the account reaction kinetics. During the titration experiments it was observed that pH of solution gradually changed with time after NaOH addition, but waiting until it reaches a constant value was not possible. It is also important to note that the SGW model does not take into the account co-precipitation and adsorption of heavy metals on iron and aluminium hydroxides, which significantly affects solubility of metals and their dissolved concentrations [63], [68]. Results of previous studies show that Fe precipitation has a capacity to remove As and Cr from water [63], as well as Cd, Zn, Cu, and Pb [68], while precipitation of Al could remove Cu and Si [63].

Apart from hydroxide consumption, SGW was also used to plot theoretical curves of metal hydroxides solubility, which are presented in Appendix 1. These curves show the theoretical lowest possible limit of concentrations that could be achieved using hydroxide precipitation for metals removal from AMD. They also show pH at which precipitation starts, which is important if selective removal of metals is desired.

### 5.2.2 SolGasWater sulfide precipitation model

Several sulfide precipitation scenarios were modelled using SGW. Based on literature data it was expected that solubility of metal sulfides will be significantly lower than that of hydroxides [8]. The results of sulfide precipitation modelling are shown in the Appendix 2. Five models were simulated to analyse behaviour of metals in AMD after sulfide

addition. Assumed concentration of the main components (based on the ALS laboratory analysis results) and sulfide dose for each of the scenarios are shown in the Table 10 below. Since Al and Cr do not form sulfides in ambient conditions they were not included in these calculations.

*Table 10. Sulfide precipitation scenarios, metals concentrations in AMD and respective sulfide doses.*

| | Scenario number | | | | |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 |
| Element | Millimolar concentration | | | | |
| Fe | 2.4 | 0 | 0 | 0 | 0 |
| Mn | 0.0835 | 0.0835 | 0.0835 | 0.0835 | 0.0835 |
| Cu | 0.39 | 0.39 | 0.39 | 0.39 | 0 |
| Zn | 1.24 | 1.24 | 1.24 | 1.24 | 1.24 |
| Cd | 0.0017 | 0.0017 | 0.0017 | 0.0017 | 0.0017 |
| Ni | 0.0016 | 0.0016 | 0.0016 | 0.0016 | 0.0016 |
| Co | 0.0053 | 0.0053 | 0.0053 | 0.0053 | 0.0053 |
| Pb | 0.0004 | 0.0004 | 0.0004 | 0.0004 | 0.0004 |
| **$HS^-$** | **4.1225** | **1.7225** | **2.5838** | **0.39** | **1.24** |

In scenario 1 sulfide amount added was equal to the sum of molar concentrations of all metals present in the solution. It was observed that compared to solubility of metal hydroxides, solubility of sulfides is significantly lower, which correlated well with the literature data [8], [69]. The results showed that iron does not react with sulfide, and starts to precipitate as $Fe(OH)_3$ at pH 3. Based on these results, for the scenario 2 sulfide concentration was decreased for stoichiometric precipitation of all metals except Fe. As in the first scenario, Fe did not form compounds with sulfide, and most of it was consumed for ZnS precipitation. Since in the scenario 2 there was considerably less $H_2S$ and free $HS^-$ in the solution, solubility of metals increased slightly. For the scenario 3 amount of sulfide was increased, and was equal 1.5 times total concentration of all metals except Fe. The solubility slightly decreased compared to scenario 2, but was still higher than in scenario 1, since the total amount of free sulfide was lower. Comparing all three scenarios, it could be concluded that for the purpose of treating water to the required levels it will suffice to add sulphide in stoichiometric or slightly higher dose to precipitate all metals except iron. Overdosing of sulphide can cause formation of toxic $H_2S$ gas, which is undesirable, and will increase operational costs, while not improving the treatment efficiency in a significant way [9]. In the scenario 4 sulfide was added only to remove Cu from water that was already free from Fe. Figure 7 in the Appendix 2 shows that Cu would be precipitated together with Pb at low pH, but since concentration of the latter is very low, it will not have significant effect on purity of copper precipitate. The last scenario was meant to evaluate possibility of selective ZnS removal. It showed that despite stoichiometric addition of sulfide for Zn precipitation, Pb and Cd have lower solubility than Zn, and therefore there was not enough sulfide to achieve minimum ZnS solubility. So compared to Cu, higher pH and more than stoichiometric addition of sulfide is required for complete Zn removal, but it would still contain impurities of Pb and Cd.

### 5.2.3 SolGasWater modelling results summary

Modelling results presented above show that hydroxide precipitation does not allow to achieve the proposed environmental requirements, as solubility of metal hydroxides is higher than the limit values. On the other hand, solubility of metal sulfides is significantly lower and provides an opportunity to comply with proposed requirements. However, Al and Cr do not form sulfides, and it was shown that Fe and Mn precipitate as hydroxides during sulfide addition. The comparison of hydroxide and sulfide solubility of metals is shown in the Appendix 3. Based on this modelling data it was decided to conduct a series of screening experiments to test different neutralization agents and sulfide sources to find most promising treatment methods.

## *5.3 Screening tests*

Applied doses of reagents and results of experiments are shown in Appendix 5. Cells coloured in pink indicate values below the proposed discharge requirements.

After a literature review and modelling a series of screening experiments was made in order to determine most promising treatment options for Kristineberg AMD based on the proposed environmental discharge requirements for As, Cd, Cr, Cu, Ni, Pb, and Zn. The tests were aimed to study four kinds of processes, namely neutralization, sulfide precipitation, neutralization combined with Fenton's reagent treatment, and Fenton reagent followed by oxidation of $MnSO_4$. Before each test AMD sample was filtered through a paper-filter to remove ferric hydroxide precipitate that formed while canister with mine drainage was standing in the laboratory. Volume of samples was 200 ml or 100 ml, and unless stated otherwise reagents were dosed in liquid form to make pH control and dosing easier, and to improve distribution of reagents in solution volume. Magnetic stirrer was used for solution mixing. The samples were mixed for ca 20 min after reagent addition and left to settle for ca 1 hour. In case of two- and three-stage treatments glass fibre filter was used to filter precipitate after each stage. After final stage samples were filtered through 0.45 μm filter. Collected samples were analysed with ICP-OES in Boliden's laboratory. All metals except Fe were analysed using calibration with standard solution, while for Fe analysis semi-quantitative method was used, that did not required a standard for calibration of ICP. Results of screening tests are shown in the Appendix 5.

### 5.3.1 Neutralization

The first series of experiments involved neutralization of AMD with caustic soda, slaked lime, limestone, and magnesia milk. Four experiments were done with dry reagents and one was repeated with liquid sodium hydroxide. For some reason it was not possible to reach pH over 7 with $Mg(OH)_2$. In accordance with SGW software model and literature data, higher pH resulted in better removal of metals. Lowest pH of 6.2 was achieved with limestone, and it showed lowest metals removal rates for Co, Cu, and Zn. Removal percentages were 95% Cu and 35.9% Zn. With $Mg(OH)_2$ pH was 6.7, and it showed significantly improved removal of Cu and Zn, 99.8% and 63.1% respectively, as well as decreased Fe and Al concentrations. According to SGW hydroxide precipitation model, $Cu(OH)_2$ should not precipitate until pH reaches 6, and $Zn(OH)_2$ should not precipitate until pH 8. Therefore, it could be concluded that adsorption and/or co-precipitation with Fe and Al hydroxides play mayor role in Zn and especially Cu removal from the solution. It also explains decrease of Pb, and Cd concentrations at pH below 7. Arsenic and Cr

were not detected in any of the samples, which signifies that they were adsorbed by Fe and Al hydroxides.

At higher pH, achieved with sodium and calcium hydroxide, it was possible to remove Cd, Cu, Ni, Pb, and Zn below detection limit of the equipment. The results also showed that best aluminium removal could be achieved at pH ca 6.7, while at high pH levels dissolved Al concentration increases. This correlates well with SGW model prediction.

The difference in results of using solid and liquid NaOH could be due to the fact that they were measured at different days, therefore calibration of the equipment was different, final pH of the solution was different, and in case of liquid reagent dilution with nitric acid was performed before analysis. Different reaction time, pipetting errors, and poor mixing of sample could have also affected the results. Thus, the results of these analyses are inconclusive as regards to which form of reagent is more efficient for metals removal, and what are the lowest concentrations that could be reached using neutralization alone.

### 5.3.2 Sulfide precipitation

The second series of experiments was devoted to studying combined hydroxide and sulfide precipitation. For neutralization tests caustic soda was selected, as it allows reaching pH values over 9. And unlike slaked lime, it does not have adsorptive properties, so it would not interfere with the results obtained by sulfide precipitation. As sulfide source three reagents were used, namely sodium sulfide, sodium hydrosulphide, and organosulfide TMT15® – liquid reagent produced by Evonic Industries AG. NaHS and $Na_2S$ used for these tests were industrial grade, so precise concentration and impurities content are unknown. Sulfide reagents are easily oxidized in contact with air, which results in formation of thiosalts and decrease of sulfide concentration in the solid reagent. Hence, dosing of sulfide was done according to pH values and based on visual observation of precipitate formation. In case of TMT15® the required dose estimated with a calculator available at the manufacturer's website was lower than required to precipitate metals efficiently, which was determined by samples analysis.

Sulfide was added as a first stage, as according to the SGW model when excess sulfide is present in water precipitation of metals should occur at low pH. The precipitate was filtered through a glass fibre filter and NaOH was added to increase pH of the solution to ca 9.5. Aliquots were taken for analysis and filtered through 0.45 µm filter after each treatment stage.

When sulfide was added to AMD as a first treatment stage without pH adjustment, low doses of $Na_2S$ and NaHS resulted in formation of brown particles. These particles changed colour to black with increase of sulfide addition and floc size. This colour change corresponds well with literature data that describes similar behaviour as formation of copper sulfide [70]. TMT15® addition resulted in formation of brown, but never black precipitate. After filtration through paper filter a lot of particles went through, which is a common problem with metal sulfides, as their particle size is very small [70], [71], [72]. Micro glass fibre filter showed better efficiency in particles retention, producing transparent filtrate with almost no suspended solids. As a second step filtrate was treated with NaOH to remove residual metals and manganese, and adjust pH. However, as soon as base was added to the filtrate black precipitate formed again, which shows that not all metal sulfides were precipitated at low pH. After pH was increased to over 9.5 precipitate

settled down with black sulfide particles on the bottom and orange hydroxide sludge on top of them (Figure 13). In some tests it was also observed that neutralization after sulfide addition resulted in formation of greenish precipitate. It could be due to consumption of sulfide by ferric iron and its reduction to ferrous at low pH. Ferrous iron hydroxide then settles at pH higher than 6 and gives the green colour. This excessive consumption of sulfide should be avoided, so removing Fe and Al prior to sulfide precipitation is desirable.


*Figure 13. Precipitate formed after sulfide addition, filtration, and hydroxide precipitation.*

One test was done to see how addition of slaked lime would decrease final metals concentrations (tests No. 3.2, Appendix 5). Sodium hydrosulphide was selected as the most efficient sulfide source, and less of it was added compared to test No. 2.3. The final concentrations were exceptionally low.

Several tests were also done with base addition as a first stage, followed by sulfide precipitation, but their analyses are not included in this work. When neutralization was done as a first treatment stage to remove Fe and Al, orange precipitate of iron and aluminium was filtered out with micro glass fibre filter. After sulfide addition formed precipitate was light brown, yellow, or light green, but never black. It could signify that most of the copper was co-precipitated with iron and aluminium, or that the black coloured particles were iron sulfide. However, according to the SGW model described above iron should not form solid compounds with sulfide in this setting. Moreover, some researches showed that pyrrhotite or troilite (FeS) only form at pH between 3.6 and 5.7 [8], so it is not likely to be observed after sulfide addition to AMD with initial pH 2.6. Sludge analysis was not performed on any of the samples, so it is not possible to say exactly what minerals were formed during precipitation. The results of these tests were inconclusive, as final pH was increased to 10 in order to remove Mn, so the results could not be compared to the results of tests described above. They did show removal of Cd, Cr, Co, Pb, and Zn below the detection limits of the equipment. However, removal of Ni was worse compared to treatment where sulfide precipitation was used prior to base addition. But it could be also due to the fact that these samples were diluted with nitric acid prior to analysis.

### 5.3.3 Neutralization combined with Fenton's reagent treatment

The third series of experiments was aimed to investigate how using Fenton's reagent as a polishing step after neutralization can improve removal of residual trace metal concen-

trations, especially cadmium. For these experiments 800ml of AMD was treated with addition of slaked lime to pH 9.5 (it later decreased to 9.3). Slaked lime was selected due to its cost advantage and the fact that unreacted lime has high adsorption capacity. Moreover, it is currently used at Kristineberg water treatment plant. After neutralization, the solution was filtered through micro glass fibre filter to remove suspended solids. An aliquot was then taken for analysis. Then pH of solution was decreased to about 6.5 with 0.1M sulphuric acid and water was divided into 3 samples 200 ml each. Each sample was then treated with different dose of iron and hydrogen peroxide. Selected iron doses were 25, 50, and 100 mg/l $FeSO_4$ based on recommendation of Boliden's water treatment experts. According to the Eq. (31) of Fenton reaction, two moles of ferrous iron are required per one mole of peroxide. However, it could be beneficial to use more than stoichiometric dose of peroxide to allow for oxidation of other metals as well. Therefore, the selected doses of peroxide were double the dose required for iron oxidation. The pH for Fenton reaction was between 3 and 4. It was hard to control pH precisely during the reaction, as both $FeSO_4$ and $H_2O_2$ decrease pH of solution. After peroxide addition formation of orange precipitate was observed (Figure 14). Samples were taken ca 20 minutes after Fenton treatment and filtered through 0.45 µm filter. Then using slaked lime pH was increased first to 9, and then to 10, and after it stabilized samples were taken and filtered for future analysis.

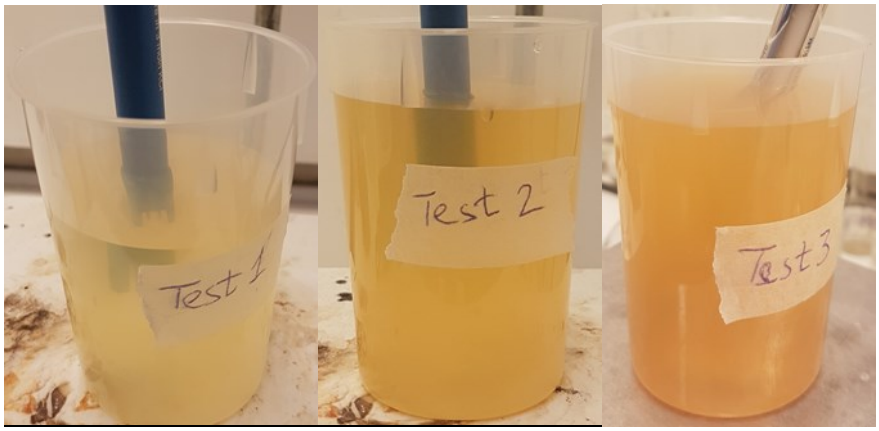


*Figure 14. Samples colour after Fenton treatment with three different iron and hydrogen peroxide doses (from left to right 25, 50, and 100 mg/l $FeSO_4$).*

The analysis of water after neutralization showed removal of As, Cr, Ni, and Pb below the detection limits, while concentrations of Cd, Cu, and Zn were below 1 µg/l. Analysis of samples after Fenton treatment showed increased concentrations of almost all elements in the solution. This could be due to contamination of water with reagents, as $FeSO_4$ used was industrial grade, and both iron sulfate and hydrogen peroxide were prepared long time before the experiments and presumably using tap water. Another explanation could be the fact that before analysis water after neutralization was filtered through a 0.45 µm filter and for the experiments it was only filtered through a fibre-glass filter. Thus there were higher concentrations of metals in the water before Fenton treatment than results of neutralization test No. 4.0 indicate. It does not explain changes in As concentration and why it was so high through the experiments. This could be due to contamination or measuring errors. It was also noticed that after Fenton treatment a lot of small suspended particles of Fe hydroxide with metals adsorbed on them went through 0.45 µm filter membrane, as filtrate had yellowish colour. This certainly affected the analysis of dissolved

metals concentrations. For these reasons it is not possible to make definitive conclusions about efficiency of Fenton treatment based on these analyses.

However, results show that after addition of slaked lime there is a clear decrease in metals concentrations. All metals were removed below the required values, while As concentration was still very high. There was no evidence that pH 10 is better for Cd removal than pH 9, but it could be due to insensitivity of equipment for low Cd concentrations. Overall, Fenton treatment results showed lower Cd concentrations compared to using lime treatment alone.

### 5.3.4 Fenton reagent followed by oxidation of $MnSO_4$

The fourth series of screening tests was performed to analyse two-stage process consisting of Fenton treatment followed by oxidation of manganese sulfate with sodium persulfate. These experiments were inspired by Veolia's Metclean$^{TM}$ treatment process, described in the Section 2.3 Commercial methods. In these experiments no microsand was used. For the first treatment stage different doses of Fenton reagent were used, and pH was kept around 4 with NaOH. Sodium hydroxide does not have the adsorption properties that unreacted lime has, so it allows to see how much metals are removed by Fenton alone. Iron dosages were 50 and 150 mg/l $FeSO_4$. More than stoichiometric amount of peroxide was added. After about 20 min pH was increased to 5.2 to precipitate residual Al and prevent its resolubilization at higher pH. After ca 20 minutes of settling samples were filtered for analysis. Solution was filtered through a glass fibre filter and its pH was increased to 8.6 with NaOH. Then $MnSO_4$ was added followed by addition of $Na_2S_2O_8$. It was decided to use sodium persulfate, as addition of chlorine to treated mine water is undesirable. Two combinations of reagents doses were tested. After ca 20 min solution was filtered through glass fibre filter and aliquot was taken for analysis. Afterwards pH was increased to 10 to see if that would improve cadmium removal. One test was also done to see if addition of peroxide alone would results in the same effect as application of Fenton reagent to AMD (test No. 5.4, Appendix 5).

The results of analyses after Fenton treatment and addition of peroxide alone are in the same range. It did not seem like application of ferrous iron oxidation as a first treatment stage has significant effect on metals removal. Chromium was removed below the detection limit in all the samples, and in all except one Pb was not detected. However, concentrations of As, Cd, and Ni were almost the same as in untreated water. Slight decrease of Co, Cu, and Zn concentrations could be seen. After precipitation of $MnO_2$ concentrations of all metals decreased, which could be partially due to increase of pH and formation of metal hydroxides. But their residual concentrations were slightly below the values predicted by SGW model. It signifies that metal cations were adsorbed by formed $MnO_2$ or co-precipitated with it. Subsequent increase of pH to 10 with NaOH resulted in further decrease of metals concentrations, though in none of the cases the proposed requirements were achieved for all the parameters. Concentrations of Cu and Zn were above the required limits in all samples. Generally, the results were worse than those of any other treatment method described above. It could be due to small particles formation and their presence in filtrate before analysis, or reagents dosages being not optimal.

### 5.3.5 Screening tests summary and choice of treatment methods

Results of screening tests are shown in the Appendix 5. All samples from the screening tests were analysed with ICP-OES at Boliden's laboratory. Some samples required dilution with nitric acid, as even after filtration through 0.45 μm filter some particulate matter was still present in the solution and was blocking nebulizer. The factors that could have affected the analysis include reagents purity, pipetting errors, contamination (e.g. from glassware and pH electrodes), sample volume, mixing speed and time, differences in final pH, which was hard to control, sedimentation time and precipitate aging, amount of precipitate smaller than 0.45 μm filter, sensitivity of ICP and its calibration.

Though it is hard to make definitive conclusions regarding efficiency of each treatment method based on the screening tests results, they gave an insight into the mechanisms behind metals removal from water. The results showed that neutralization alone removes metals to concentrations below predicted by SGW model. But for some metals, such as Al, Cu, and Zn, the model is useful for prediction of pH at which solubility is at its minimum. As it could be seen from the results, most of the analyses showed undetectable concentrations of Cd, Cr, and Pb. It could be attributed to the relatively low sensitivity of ICP-OES equipment used and initially low concentrations of those elements. However, the fact that metal concentrations were below the saturation concentrations of those metals at the given pH range evidences adsorption of metals on Fe(III) oxy hydroxysulfate and Al hydroxysulfate, that has been reported in the literature [48], [63], [64]. The screening tests also showed that using base addition most of the Cu is removed at pH below 7, meaning that it is adsorbed on Fe or Al hydroxides.

Based on the results discussed above three treatment methods were selected for further investigation during the main experiment series. The summary of selected treatment methods is shown in the Table 11 below. Justification for selection of these methods is presented below.

*Table 11. Treatment methods selected for the main experimental series.*

| Method description | Number of stages | Reagents |
|---|---|---|
| Neutralization for Fe and Al removal followed by sulfide precipitation and final pH adjustment | 3 | $Ca(OH)_2$, NaHS |
| Neutralization followed by Fenton reagent | 2 | $Ca(OH)_2$, $FeSO_4$, $H_2O_2$ |
| Neutralization followed by manganese oxidation | 2 | $Ca(OH)_2$, $MnSO_4$, $H_2O_2$ |

The first selected treatment is three-stage process, consisting of $Ca(OH)_2$ neutralization for Al and Fe removal followed by sulfide precipitation with NaHS, and subsequent lime addition for pH adjustment and polishing. Even though this method was not tried during the screening tests, it seems promising for the following reasons:

a. Removing Fe and Al before sulfide addition would decrease sulfide consumption;

b. Previous research showed that in comparison to sulfide precipitation, precipitation of hydroxides followed by sulfides requires less NaHS. Hence cost savings and less of toxic regent required [69];
c. There exists successful ChemSulphide® technology that operates based on this treatment method;
d. Lower sludge volumes compared to traditional lime precipitation;
e. Production of potentially valuable ZnS product (with low impurities of copper and other metals), which could be put through concentrator or smelted directly;
f. Produced lime sludge would contain less toxic metals, and therefore would be easier to dispose. Additional tests would have to be done to estimate its stability, physical and chemical properties. It could possibly be suitable for leaching to obtain copper product;
g. Aluminium and Fe would be removed at the pH level where they are least soluble;
h. Lower solubility of sulfides at a wide range of pH would ensure low effluent concentrations.

However, the disadvantages of this method include the following:

a. Toxicity of sulfides, difficulties with their handling, and difficulties of dosing control;
b. Excessive addition of sulfides could result in harmful $H_2S$ gas release;
c. Addition of sulfides could increase amount of sulfates in the effluent. So addition of ettringite process might be required is sulfate removal is needed;
d. Excess sulfide dosages could lead to thiosalts formation in the effluent;
e. Typically sulfide precipitate consists of very fine particles that hinder solid-liquid separation, but polymer addition could solve this issue.

The second treatment method selected was Fenton reagent as polishing step after neutralization. Boliden Mineral AB already has several Fenton treatment plants in operation in different locations, and has in-house developed technology for building new Fenton plants. This method would not require significant changes in the existing treatment process, which already shows good rate of metals removal. It could be added as a polishing step, with an aim to ensure lower metal concentrations in the effluent. The advantages of the proposed process include the following:

a. Relatively inexpensive and non-hazardous reagents;
b. The technology is proven to be effective for metals removal and is widely used in the world and by Boliden Mineral AB;
c. Schwertmannite and ferrihydrite are working well for adsorption of anions, such as arsenate ($AsO_4^{3-}$) and chromate ($CrO_4^{2-}$);
d. Sludge after lime precipitation could be leached to obtain valuable metals;
e. Polishing stage would be easy to add to the existing treatment train;

The disadvantages of Fenton reagent treatment method include the following:

a. High volume and bad properties of gypsum sludge, difficulties in dewatering, transportation, and storage;
b. Large volumes of iron hydroxide sludge that contains toxic metals, which is hard to dispose;

c. Acid addition to water is required in order to decrease pH back to about 4-6 after lime treatment, which creates costs and increases sulfate content in water;
d. Alkali addition is required after Fenton treatment to precipitate the residual metals as hydroxides and increase pH back to about 9.5;
e. Currently no requirements for Al levels in effluent are anticipated, however, it is important to take Al concentrations in the account. During lime precipitation at high pH Al could resolubilize;
f. Sludge obtained after Fenton treatment would likely not have commercial value as it would contains low concentration of metals and high concentration of iron;
g. Polymer addition might be required for effective floc formation and precipitation of the sludge;
h. Possible increase of Fe content in the effluent;
i. Increase of sulfate content in water from added ferrous sulfate.

The third treatment method selected for further tests was neutralization of AMD with lime followed by polishing step of $MnSO_4$ oxidation with $H_2O_2$. Peroxide was used due to its capacity to produce hydroxyl radicals with high oxidation potential and decomposition to environmentally friendly compounds – oxygen gas and water. As in case of Fenton, this method could serve as a polishing step for further decrease of metal concentrations in the effluent. The advantages of the proposed process include the following:

a. Relatively inexpensive and non-hazardous reagents;
b. Compared to using Fenton as a polishing step, Mn oxidation does not require decrease of pH to 4, as it works best at pH ca 8.6. Therefore, the process requires no acid reagent. It also would consume less alkali, as after Fenton pH needs to be increase from 4 to 9.5, and in this case it would be increased only from 8.6 to 9.5;
c. Mn works well for base metals cations precipitation, e.g. Cu and Zn, while Fenton works better for As and Cr anions removal by co-precipitation and absorption;
d. Sludge after lime precipitation could be leached to obtain valuable metals;
e. Polishing stage would be easy to add to the existing treatment train;

However, this method has a number of disadvantages, similar to those of Fenton:

a. High volume and bad properties of limed sludge, difficulties in dewatering, transportation, and storage;
b. Large volumes of manganese hydroxide sludge that contains toxic metals, which is hard to dispose;
c. Boliden already has several Fenton plants in operation, and has the knowledge to build new ones. Developing and testing Mn oxidation plant could take some time.
d. Possible Al resolubilization at high pH;
e. Polymer addition might be required for effective floc formation and precipitation of the sludge;
f. Possible increase of Mn content in the effluent and increase of sulfate content.

For the main tests slaked lime was selected as a neutralization agent due to its advantages over other reagents under the study, described in detail in the Section 2.2.1. Lime is currently used at Kristineberg water treatment plant, and allows achieving pH 9.5 in the effluent. The drawback of using slaked lime is the necessity of auxiliary equipment for slaking.

## 5.4 Main experiments

The three series of main experiments were designed using MODDE 8.0 software for design of experiments (DOE). DOE is an approach for organization of experimental work, which aids to select a smallest possible set of experiments that would determine relationship between factors affecting a process and output of the process. After experiments are performed and data is input in the software, MODDE constructs a predictive model that shows effect of factors and their interactions on the process output. The model then could show the optimum combination of factor setting for a desired process output. DOE could be used for three objectives [73], [74]:

1. Screening – to determine which factors are the most influential on the process output and at what range;
2. Optimization – to find the optimum setting for the process;
3. Robustness testing – to determine whether robustness of the process to small fluctuations in factor levels could be guaranteed close to the optimum point or should specifications be changed in order to achieve it.

Another method to conduct experiments is COST approach – change one single variable at a time. Compared to DOE, COST approach does not allow estimation of factor interactions influence on the process. Moreover, COST makes it difficult to assess systematic and unsystematic variability (i.e. effects and noise). Furthermore, the advantage of DOE is that it can produce response counter plot of the investigated system, which shows a best direction in which factors should be changed to find the optimum [74].

For the main tests DOE approach was used with screening design objective, as it requires minimal number of test runs and is typically applied when factors range is unknown and their importance unclear. Full factorial design was selected with 2 levels, as only two controlled factors were used for each model. The design is orthogonal (balanced) and consisted of all combinations of the factor levels, with estimated effect of one factor being independent of the effects of the other factor. PLS method (partial least squares regression) was used to fit the model. As responses concentrations of metals in the treated water were selected. Each main experiment therefore consisted of 4 design runs and 3 centre point runs (CP) though for Mn oxidation only 2 centre point experiments were done.

### 5.4.1 Three-stage treatment with lime and NaHS

The selected treatment consisted of three stages, namely pH adjustment for precipitation of Fe and Al, NaHS addition for precipitation of ZnS and other metal sulfides, and lime addition for pH adjustment and polishing.

For experiments design two factors were selected. First factor was the pH before sulfide precipitation. As described in Section 5.2.1 SolGasWater hydroxide consumption model, Fe(III) and Al hydroxides precipitate at different pH levels. The aim of varying the pH was to see how much metals how much of Fe and Al remain in the solution at pH levels between 4 and 5, and how much metals are adsorbed on Fe(III) and Al hydroxides, as these affects the subsequent sulfide precipitation. The second factor was concentration of sulfide as NaHS dose added during the second stage. NaHS was added as 0.8 M solution. The concentration of NaHS was varied between 0.675 and 2.025 mmol NaHS to 1 litre

AMD (0.05-0.15 g/l NaHS). These values were selected based on the SGW sulfide precipitation model (Section 5.2.2) and results of screening tests. It is important to note here that the SGW model was done for sulfide addition to AMD without preliminary lime treatment. The summary of experiments is presented in the Table 12 below.

*Table 12. Three-stage treatment experiments. Reagents doses and pH.*

| Test No. | pH after first stage neutralization | ml $Ca(OH)_2$ 0.8M /500ml | pH after $Ca(OH)_2$ | g NaHS / l AMD | mmol NaHS / l AMD | pH after NaHS and filtration | ml 0.8M $Ca(OH)_2$ / 500 m | Final pH |
|---|---|---|---|---|---|---|---|---|
| 1 | 4.2 | 0.8 | 4.3 | 0.05 | 0.675 | 4.5 | 4.1 | 9.2 |
| 2 | 4.2 | 0.8 | 4.3 | 0.15 | 2.025 | 4.3 | 4.1 | 9.3 |
| 3 | 4.6 | 2 | 5.7 | 0.1 | 1.350 | 5.8 | 0.7 | 9.2 |
| 4 | 4.6 | 2 | 5.6 | 0.1 | 1.350 | 5.5 | 1.1 | 9.1 |
| 5 | 4.6 | 2 | 5.6 | 0.1 | 1.350 | 5.4 | 1.1 | 9.4 |
| 6 | 5.2 | 0.7 | 6.6 | 0.05 | 0.675 | 6.6 | 0.6 | 9.3 |
| 7 | 5.2 | 0.4 | 6.3 | 0.15 | 2.025 | 6.7 | 0.4 | 9.4 |

Three batches of AMD treated with lime were prepared for three levels pH before sulfide addition (first controlled factor). Due to difficulties in precise pH control the pH levels after lime treatment were 4.2, 4.6, and 5.2. Water after lime treatment was left to sediment for approximately 24 hours. Then it was filtered through a glass fibre filter. Aliquot was taken from each batch for analysis. For experiments 500 ml samples were taken and lime was added to increase pH before NaHS addition, as higher pH results in better metals removal. It was planned to increase pH to 3 different levels, but due to differences in pH control tests 6 and 7 had different pH before NaHS. Magnetic stirrer was used for reagents mixing. After addition of NaHS solution was mixed rapidly for about 5 min and then slowly for about 15 min before it was let to settle for around one hour. Then samples were filtered through a glass fibre filter to remove most of the suspended solids, but since metal sulfides form very fine particles, samples were then filtered again through 0.45 µm filter. Aliquot was then taken for analysis, and the remained solution was treated with lime. After lime addition solution was mixed rapidly for about 5 min and then slowly for about 15 min before it was let to settle for around one hour. Then it was filtered through 0.45 µm filter and saved for analysis.

### 5.4.2 Lime neutralization followed by Fenton reagent

As described in the Section 2.2.3 Fenton reagent, reaction of $FeSO_4$ and $H_2O_2$ at pH about 3-5 results in precipitation of Fe(III) hydroxide, which removes ions of metals and metalloids by co-precipitation and adsorption.

During the design of Fenton reagent experiment 2 factors were selected, namely concentration of $FeSO_4 \cdot 7H_2O$ added, which varied from 30 to 100 mg Fe to 1 litre AMD, and concentration of $H_2O_2$, which was varied between 2 and 2.5 moles of per mole of $FeSO_4 \cdot 7H_2O$. The concentration was selected to be several times higher than stoichiometrically required to make sure that all iron is completely oxidized. The summary of experiments is presented in the Table 13 below:

*Table 13. Fenton treatment experiments. $FeSO_4$, $H_2O_2$, and lime doses.*

| Test No. | Initial pH | mg Fe/l AMD | $H_2O_2$:Fe molar ratio | pH after $FeSO_4$+$H_2O_2$ | ml 0.8M $Ca(OH)_2$ /150 ml | Final pH |
|---|---|---|---|---|---|---|
| 1 | 8.8 | 30 | 2:1 | 3.7 | 0.4 | 9.5 |
| 2 | 8.8 | 30 | 2.5:1 | 3.6 | 0.6 | 9.3 |
| 3 | 8.8 | 65 | 2.25:1 | 3.3 | 0.7 | 9.5 |
| 4 | 8.7 | 65 | 2.25:1 | 3.3 | 0.7 | 9.3 |
| 5 | 8.6 | 65 | 2.25:1 | 3.4 | 0,7 | 9.3 |
| 6 | 8.9 | 100 | 2:1 | 3.3 | 1.1 | 9.4 |
| 7 | 8.8 | 100 | 2.5:1 | 3.3 | 1.3 | 9.4 |

For these experiments a batch of lime neutralized water was prepared, which ensured that water quality before Fenton treatment is the same for all test runs. Lime was added to AMD to pH 9.5, after which it was left to mix for about 30 min and then to settle for about 24 hours. Then water was filtered through a paper filter to remove suspended particles. A 150 ml volume of lime neutralized water was used in each experiment. Initial pH of water was about 8.9 (it decreased from 9.5 presumably due to slow precipitation of residual metal hydroxides). Using 0.01 M sulphuric acid pH was adjusted to around 6.0. Then it further decreased to required level of about 3.5 after $FeSO_4$ and $H_2O_2$ addition. Magnetic stirrer was used for mixing the solution. First Fe was dosed as 40 g/l $FeSO_4 \cdot 7H_2O$ solution and then $H_2O_2$ was dosed as 3.3% solution from a pipette. The solution was then mixed at moderate speed for about 10 min and at low speed for about 20 min. Formation of yellow-orange precipitate was observed. Then lime was added to the solution to reach pH 9.5, but it was gradually decreasing after it, so final pH varied through the experiments. No polymer was added to improve sedimentation. After around 20 min of mixing solution was left to settle for about an hour before being filtered through 0.45 µm filter and stored for analysis.

### 5.4.3 Lime neutralization followed by Mn oxidation

As described in Section 2.2.4 Manganese sulfate oxidation, several oxidizing agents could be used to oxidize $MnSO_4$ and obtain precipitate of $MnO_2$, which has high adsorption capacity for base metals removal. Oxidizing agents that were considered for this series of experiments included NaClO, $Na_2S_2O_8$, $KMnO_4$, and $H_2O_2$. The advantages and disadvantages of these oxidants are described in the Section 2.2.4. Rapid tests were done with each of these oxidants to observe how they react with $MnSO_4$.

The tests showed that $MnSO_4$ readily reacts with $KMnO_4$ producing dark brown precipitate. However, at alkaline pH>8.5 addition of NaClO, $Na_2S_2O_8$, and $H_2O_2$ at higher than 1:1 molar dose did not cause the reaction of $MnO_2$ formation until lime or NaOH was added to the solution. As discussed in the Section 2.2.4 Manganese sulfate oxidation, oxidation of Mn(II) has low kinetic rate and could take up to several days without presence of catalyst. After alkali addition to the sample with $MnSO_4$ and oxidant, formation of brown flocs was observed which were changing colour to more dark brown with time. Flocs were rather big, but were not always settling well, which could be seen at the Figure

15 and Figure 16 below. Flocs formed after permanganate addition were the biggest, though not all of them settled and some were attached to walls. Oxidation with hypochlorite resulted in formation of small particles, which settled rather well. Particles after persulfate addition were also small, and after filtration through 0.45 µm filter solution filtrate had colour. After oxidation with peroxide smallest fines were formed, which did not settle and stayed suspended in the solution. Residual concentrations of metals in these samples were not measured.

*Figure 15. Precipitate of $MnO_2$ 33 minutes after addition of 200 mg $MnSO_4$ per litre neutralized AMD and its oxidation with $Na_2S_2O_8$ (1:1.5 molar ratio).*

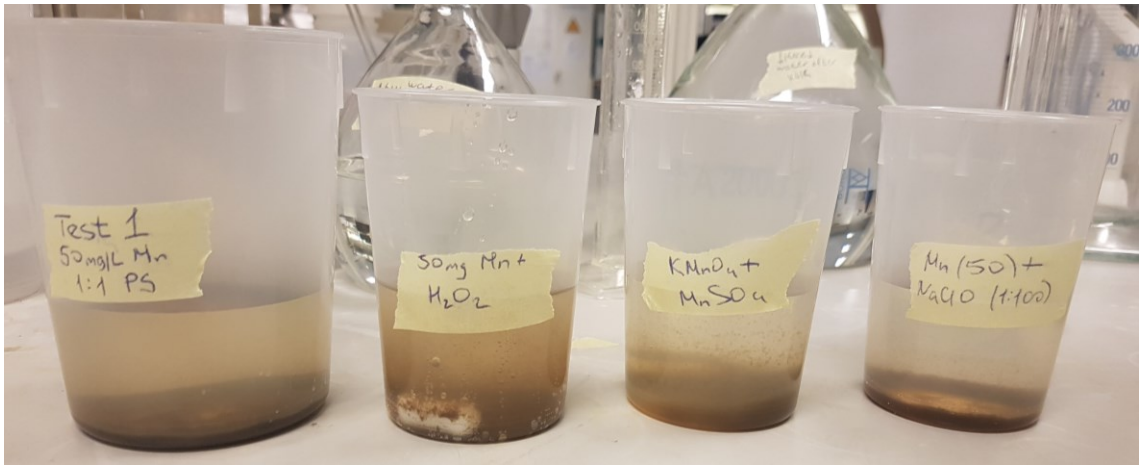


*Figure 16. Precipitate of $MnO_2$ obtained after oxidation of 50 mg $MnSO_4$ per litre with different oxidants, left to right $Na_2S_2O_8$, $H_2O_2$, $KMnO_4$, and NaClO.*

The issue with flocs settling could be due to formation of small bubbles that attach to flocs and carry them to the surface, or too high oxidation-reduction potential of water after oxidant addition. Further investigations are required to select optimal oxidant dose and flocculation aid.

After the tests hydrogen peroxide was selected to be an oxidizing agent based on the fact that it decomposes to water and oxygen gas, thus not producing secondary contaminants.

During the design of $MnSO_4$ oxidation experiments 2 factors were selected, namely concentration of $MnSO_4 \cdot H_2O$ added, which varied from 50 to 200 mg Mn per 1 litre AMD, and concentration of $H_2O_2$, which was varied between 2 and 3 mole peroxide per mole of $MnSO_4 \cdot H_2O$. Two experiments were also done to see if combination of $MnSO_4$ and lime would work without addition of oxidizing agent. Preliminary tests showed formation of brown flocs of $MnO_2$ after addition of $MnSO_4$ and lime or NaOH. Concentration of Mn was selected to be 50 and 125 mg/l and final pH was adjusted to about 9.5. The test procedure was the same as described above, and same water after lime treatment was used. The summary of experiments is presented in the Table 14 below.

*Table 14. Manganese oxidation experiments. $MnSO_4$, $H_2O_2$, and lime doses.*

| Test No. | mg Mn/l AMD | $H_2O_2$:$MnSO_4$ molar ratio | ml of 0.8M $Ca(OH)_2$ /150 ml | Final pH |
|---|---|---|---|---|
| 1 | 50 | 2:1 | 0.3 | 9.7 |
| 2 | 50 | 3:1 | 0.2 | 9.3 |
| 3 | 125 | 2.5:1 | 0.4 | 9.1 |
| 4 | 125 | 2.5:1 | 0.4 | 8.9 |
| 5 | 200 | 2:1 | 0.4 | 9.0 |
| 6 | 200 | 3:1 | 0.4 | 8.9 |
| 7 | 50 | No $H_2O_2$ | 0.3 | 9.5 |
| 8 | 125 | No $H_2O_2$ | 0.6 | 9.4 |

For these experiments a batch of lime neutralized water was prepared, which ensured that water quality is the same for all test runs. Lime was added to AMD to pH 9.5, after which it was left to mix for about 30 min and then to settle for about 24 hours. Then water was filtered through a paper filter to remove suspended particles. A 150ml volume of lime neutralized water was used in each experiment. Adjustment of pH to 8.6 was not done, as initial pH of solution was around 8.9 (it decreased from 9.5 presumably due to slow precipitation of residual metal hydroxides), and after addition of $MnSO_4$ and $H_2O_2$ it was decreasing slightly. Magnetic stirrer was used for mixing of solution. First Mn was dosed as 40 g/l $MnSO_4 \cdot H_2O$ solution and then $H_2O_2$ was dosed as 3.3% solution from a pipette. The solution was then mixed at moderate speed for about 5 min. No precipitate formed when both $MnSO_4$ and $H_2O_2$ were added to the solution. However, after lime was added formation of dark brown flocs of $MnO_2$ was observed. Lime was dosed to reach pH about 9.5, but it was gradually decreasing after it, so final pH varied through the experiments. After final pH was reached 0.1 ml of anionic polymer Magnafloc 10 (0.05%) was added to improve sludge precipitation. After around 10 min of mixing solution was left to settle without mixing for about an hour before being filtered through 0.45 µm filter and stored for analysis.

# 6 Results

In the present study, acidic mine drainage from Kristineberg mine in norther Sweden was subjected to several treatment methods for metals removal from water. The AMD was characterised by low pH of ca 2.8 and high concentrations of sulfate (ca 2600 mg/l), iron (ca 180 mg/l), and other metals and metalloids (ca 95 mg/l Al, 82 mg/l Zn, 48 mg/l Mn, 23 mg/l Cu, 300 µg/l Co, 190 µg/l Cd, 100 µg/l Pb, 21 µg/l As). Most of the iron in water was in ferric form, supposedly due to activity of acidophilic Fe-oxidizing bacteria.

The results of main experiments are presented in Appendices 6 and 7. Since the results of Fenton and Mn oxidation experiments showed poor repeatability, it was not possible to evaluate the results using MODDE software model. A model was made for sulfide precipitation of metals with NaHS, which showed poor validity, but allowed to get an insight into the sulfide precipitation process.

Analysis of precipitates was not performed, as it was out of scope for the present thesis work. Moreover, such analysis would be difficult to conduct due to small amount of precipitate formed during the experiments. Volume of sludge formed during precipitation and its properties were not analysed for the same reasons. Therefore, information regarding minerals that formed during precipitation is not available. The speculations regarding which minerals were controlling concentration of Fe, Al, and Mn in the solution are based on the reviewed literature data.

The results of experiments in most cases showed better removal of metals than the predictions of SGW precipitation models. These could be explained by the fact that SGW model is based on equilibrium analytical calculations, and does not take into the account such phenomena as adsorption and co-precipitation. However, as had been described above in Section 2.2.3 Fenton reagent and Section 2.2.4 Manganese sulfate oxidation, adsorption and co-precipitation play important role in metals removal from water during formation and precipitation of Fe hydroxide and Mn dioxide. Decrease in dissolved metals concentrations below their solubility level could also be attributed to co-precipitation and adsorption of metal ions on Al hydroxide and unreacted lime particles.

The results of lime treatment to pH about 9.5 prior to Fenton and Mn oxidation experiments showed that concentrations of all metals except Al, Fe, and Cu are below the solubility curves modelled in SGW presented in Appendix 1. Based on the literature data, it could be suggested that most of the As, Cr, and Pb ions are removed from the solution first during precipitation of ferric iron as schwertmannite at pH about 3-3.5 [63]. About 20% of Cu is also removed during iron precipitation. Then during precipitation of Al as basaluminite at pH about 4.2-4.7 Cu ions concentration is further decreased and some Si is removed from the solution [63]. With further increase of pH precipitation of Mn oxides at pH over 7 could have played a role in removal residual Cu and Zn, as well as Ni, Cd, and Co, as reported in the literature [19]. Manganese was reported to precipitate from mine drainage as birnessite and manganite, though no crystalline phases were detected and precipitate was fine-grained with Mn present in different valence states [19].

## 6.1 Three-stage treatment with NaHS

Comprehensive results of the three-stage treatment tests are shown in the Appendix 6. Cells coloured in pink indicate values below the proposed discharge requirements.

Together with samples after NaHS tests a sample of untreated AMD was analysed again, as while water was standing still in laboratory a lot of brown precipitate of ferric iron hydroxide has formed. After one month there was nearly 97% decreased in iron content, approximately 90% decrease in As, 80% in chrome, 20% in copper, and 55% in lead concentration. Concentrations of Al and other metals did not change significantly. Raw AMD analyses and AMD analyses after one month are shown in the Table 15 below.

As described earlier, the experimental procedure included preparation of three batches of water with different pH levels, namely 4.2, 4.6, and 5.2. Samples from these batches were analysed for total concentration. The results of analyses are presented in the Appendix 6 and in the Table 15 below. Analysis of sample with pH 4.6 showed concentrations of elements higher than in raw water, which could be attributed to presence of suspended solids in the sample, contamination, or measuring error.

*Table 15. Results of three-stage experiments, water quality after first stage lime addition.*

| Sample name | pH | Al, mg/l | As, µg/l | Cd, µg/l | Co, µg/l | Cr, µg/l | Cu, mg/l | Ni, µg/l | Pb, µg/l | Zn, mg/l | Fe, mg/l |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Raw AMD | 2.8 | 84.1 | 14.7 | 176 | 295 | 30.3 | 21.9 | 71.6 | 251 | 78.0 | 141.0 |
| Raw AMD after 1 month sedimentation | 2.8 | 87.2 | 1.6 | 182 | 286 | 6.0 | 17.7 | 86.4 | 117 | 83.6 | 4.2 |
| Test 1 after lime addition | 4.2 | 20.0 | 1.5 | 174 | 278 | <2.0 | 13.3 | 78.1 | 63 | 81.9 | 2.2 |
| Test 2 after lime addition | 4.6 | 26.2 | 9.3 | 170 | 268 | 32.9 | 16.9 | 81.0 | 315 | 79.4 | 3.1 |
| Test 3 after lime addition | 5.2 | 2.5 | 0.8 | 177 | 279 | <0.9 | 8.6 | 85.2 | 18 | 79.8 | 0.4 |

When pH was increased to 4.2 almost half of the remaining Fe and about 77% of Al were removed from the solution, as well as 25% of Cu and 50% of Pb.

Comparing samples with pH 4.2 and pH 5.2 we could see that the latter had significantly lower concentrations of Fe, Al, As, Cr, Cu, and Pb. Copper concentration has decreased by 65%. Since there was relatively small amount of iron left in the solution, copper removal at pH between 4 and 5 could be attributed to adsorption or co-precipitation with aluminium. At pH 5.2 only about 60% of the initial Cu content was left in the solution. This correlates well with the literature data on role of aluminium in the removal of metals from water [19]. However, concentrations of Cd, Co, Ni, and Zn were virtually not affected by the pH increase.

The results of sulfide precipitation are presented in the Table 16 below. Cells coloured in pink indicate values below the proposed discharge requirements. The experiments showed that only the highest NaHS dose in combination with high pH achieved complete Zn removal. But copper was removed even at lowest pH and lowest NaHS dose. Another

observation is that Ni concentrations were rather high even after last treatment stage in all the experiments. Arsenic concentrations after NaHS addition were generally lower than after lime addition to pH over 9, but never below the proposed requirements. What is also interesting to note is that concentrations of sulphur and sulfate were almost the same in all the analysed samples. In Test 7 more than stoichiometric amount of sulphide was added, yet it had no effect on residual sulphur and sulfate concentrations. This could be due to formation of $H_2S$ gas that was noticed during the experiments.

*Table 16. Results of three-stage experiments, water quality after second stage NaHS addition.*

| Sample name | NaHS dose, g/l | pH after NaHS | As, µg/l | Cd, µg/l | Cr, µg/l | Cu, µg/l | Ni, µg/l | Pb, µg/l | Zn, µg/l | S, mg/l |
|---|---|---|---|---|---|---|---|---|---|---|
| Requirements | | | 0.5 | 0.25 | 3.4 | 0.5 | 4.0 | 1.2 | 6 | |
| Test 1 | 0.05 | 4.5 | 1.6 | 2 | 5.5 | <1 | 81.0 | 0.4 | 57100 | 933 |
| Test 2 | 0.15 | 4.3 | 0.7 | <0.05 | 5.4 | <1 | 79.5 | <0.2 | 12 | 930 |
| Test 3 | 0.1 | 5.8 | 0.8 | <0.05 | <0.5 | <1 | 72.2 | <0.2 | 1420 | 933 |
| Test 4 | 0.1 | 5.5 | 0.6 | <0.05 | <0.5 | <1 | 72.8 | <0.2 | 48 | 942 |
| Test 5 | 0.1 | 5.4 | 0.7 | <0.05 | <0.5 | <1 | 70.9 | <0.2 | 153 | 940 |
| Test 6 | 0.05 | 6.6 | 0.6 | 0.08 | <0.5 | <1 | 79.3 | <0.2 | 17500 | 939 |
| Test 7 | 0.15 | 6.7 | 0.6 | <0.05 | <0.5 | <1 | 43.3 | <0.2 | <2 | 928 |

Because the tests described above showed insufficient Ni removal, it was decided to conduct three identical additional tests with higher pH. Raw water was treated with lime to pH 6.1, and after sedimentation and filtration 0.1 g/l dose NaHS was added together with NaOH to reach pH ca 8.5, which should have been sufficient for Co and Ni removal below 0.1 µg/l according to SGW sulfide precipitation Scenario 2 (Figure 1, Appendix 2). During NaHS addition pH increase was observed. The results of these tests are shown in the Table 17 below. Cells coloured in pink indicate values below the proposed discharge requirements.

*Table 17. Additional 3-stage sulfide precipitation tests for Ni removal with NaHS dose 0.1 g/l.*

| Test No. | Stage | pH | As, µg/l | Cd, µg/l | Co, µg/l | Cr, µg/l | Cu, µg/l | Ni, µg/l | Pb, µg/l | Zn, µg/l | S, mg/l |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Requirements | | | 0.5 | 0.25 | | 3.4 | 0.5 | 4 | 1.2 | 6 | |
| Unfilt. raw water | | 2.8 | 5.7 | 196 | 306 | 35 | 19400 | 89 | 191 | 87400 | 1030 |
| First stage pH adj. | | 6.1 | 0.8 | 179 | 279 | 0.9 | 4040 | 83 | 1.5 | 76800 | 997 |
| 1 | After NaHS | 8.8 | <0.5 | <0.05 | 31 | <0.5 | <1 | 47 | <0.2 | <2 | 973 |
| 1 | After lime | 9.5 | 0.7 | <0.05 | 20 | <0.5 | <1 | 41 | <0.2 | <2 | 1070 |
| 2 | After NaHS | 8.6 | <0.5 | <0.05 | 21 | <0.5 | <1 | 45 | <0.2 | <2 | 962 |
| 2 | After lime | 9.4 | <0.5 | <0.05 | 17 | <0.5 | <1 | 44 | <0.2 | 2.4 | 1080 |
| 3 | After NaHS | 8.7 | 0.7 | <0.05 | 12 | <0.5 | <1 | 42 | <0.2 | <2 | 1060 |
| 3 | After lime | 9.4 | <0.5 | <0.05 | 16 | <0.5 | <1 | 42 | <0.2 | <2 | 1080 |

As could be seen from the table above, Ni was not removed successfully. Analysing literature data on sulfide precipitation of Ni it was found that several factors could explain these results. Firstly, nickel does not react with $H_2S(aq)$ species at ambient conditions and requires bisulfide ions to be present in the solution. Therefore, alkaline pH is required for NiS precipitation. Some sources recommend pH ca 10 for high Ni removal [9], [75]. During these experiments pH was ca 8.6. Secondly, addition of more than stoichiometric sulfide could result in precipitate dissolution, so it is important to keep Ni:S ratio 1:1 [76]. Also excess sulfide addition results in formation of aqueous polysulfide species that consume excess sulfide from solution and make it unavailable for metal sulfide precipitation [77]. Thirdly, it was reported that in presence of oxygen soluble $Ni(OH)_2$ and $NiSO_4$ could form [9]. These could explain high Ni concentrations in the treated water. Therefore, additional tests are required to find optimum conditions for Ni removal.

Removal of uranium was worse compared to neutralization followed by polishing, though in most of the samples it was below the proposed requirements. Mercury was below the proposed limits already in the raw water.

### 6.1.1 MODDE model simulation for sulphide precipitation

As regards to MODDE model, there were two factors that were varied in this experiment design, namely pH after lime addition prior to sulfide precipitation and amount of NaHS added. However, there were over factors that affected the experiments, but were not included in controlled factors for the model, for example concentration of metals after Fe and Al precipitation. Experimenting with MODDE model it was found that the best model parameters are achieved using three factors: NaHS concentration after Cu precipitation (controlled), pH after NaHS addition (uncontrolled factor), and the combination of the two. Using pH before NaHS addition as a factor did not result in a good model. Using those three factors resulted in condition number for the model to be 1.378. Condition number is a measure of how spherical design is, i.e. it shows the ratio between the longest and shortest diagonals of design matrix. For a screening design it should be below 3, and closer to 1 [78]. The model was designed only for sulfide precipitation, and did not include data after last pH adjustment stage. Furthermore, model did not include all of the analysed elements, as concentrations of Cd, Cr, Cu, and Pb were below the detection limit in most of the samples. Arsenic analyses were also not included in the model because they had high measuring uncertainty. Therefore, responses of the model included only residual concentrations of Al, Co, Ni, Zn, and Fe.

Responses for Al and Zn were transformed using logarithmic transformation (10Log(C1*Y+C2)), with C1 being 1 and C2 being zero. Transforming other responses did not improve the model.

Figure 17 below shows the main MODDE model parameters. Parameter R2 shows percent of variation of the response explained by the model. The second bar shows Q2 parameter, which is the fraction of the variation of the response predicted by the model according to cross validation and expressed in the same units as R2. If both R2 and Q2 are close to 1 it is an indication of a good model. In the developed model R2 varies between 0.90 for Zn and 0.99 for Ni, and Q2 varies between 0.49 for Co and 0.93 for Al. The third bar shows validity of the model, and for a model without lack of fit it should be

over 0.25. For all the responses under the study Model Validity is over 0.67, signifying that model error range is in the same range as the pure error and there is no significant lack of fit. The last bar shows pure error, which is variation of the response under the same conditions. The closer it is to 1, the better is reproducibility of the experiments. For all the responses it is higher than 0.95.

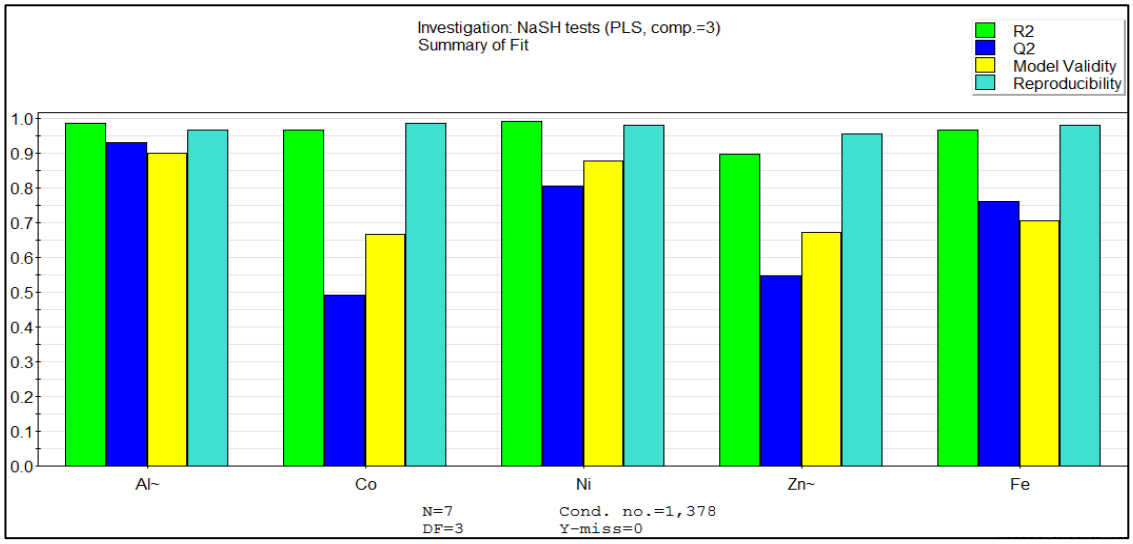


*Figure 17. MODDE model parameters of sulfide precipitation model.*

Figure 18 below shows scaled and centred PLS coefficients that could be used for model interpretation. Coefficients show response change when factor changes from 0 to +1. So the bigger the bar is, the more response changes with the change in a factor. The error bars show 95% confidence interval for a given response. Long bars indicate that measured responses had high variation, and short bars show that responses were varying in a more narrow range. If these bars cross zero, it means that the factor is not statistically significant for the model. As could be seen, the selected model factors are insignificant for some of the responses. For example, since Al and Fe do not form sulfides, NaHS dose has no effect on their residual concentration, while increase in pH results in precipitation of Fe and Al hydroxides. Arsenic was not included in SGW model, but it is known that at pH when $H_2S(aq)$ is the dominant sulphide species, arsenic could precipitate as $As_2S_3$ or $As_2S_5$. At higher pH $As^{3+}$ and $As^{5+}$ form soluble sulphide complexes. There should also be correlation between NaHS dose, pH and Zn concentration, but it can't be seen from this figure. However, all three factors are important for Co and Ni residual concentrations.

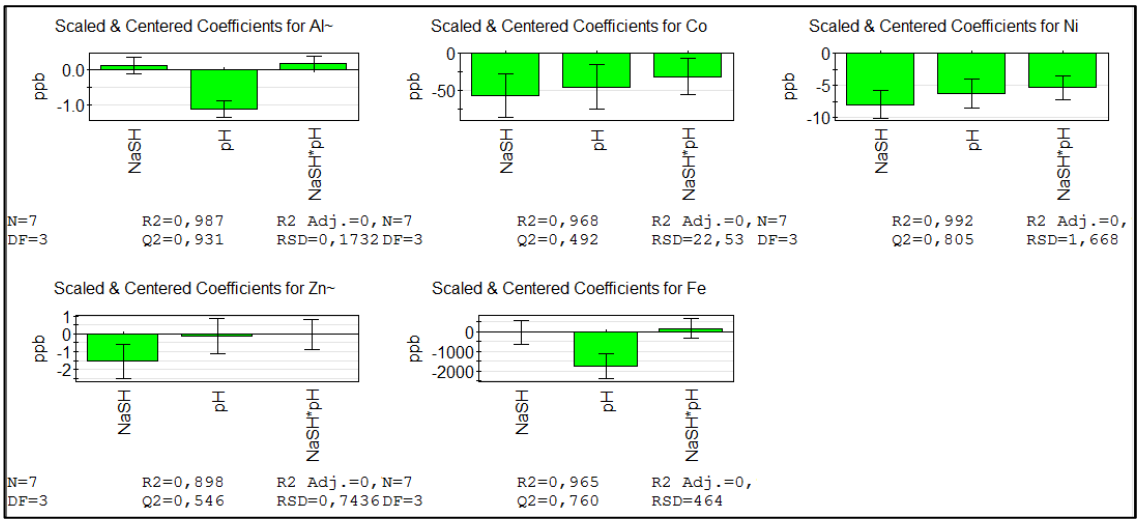


*Figure 18. Regression coefficients for all factors of the sulfide precipitation model.*

Figure 19 and Figure 20 below present the Normal Probability Plot of standardized residuals plotted on a cumulative normal probability scale. The raw residual is the difference between the observed and the fitted (predicted) value, and the standardized residual is the raw residual divided by the residual standard deviation. The plot of standardized residuals serves for detection of outliers and accessing normality of residuals. It could be seen that for all the analysed responses residuals are not lying on the straight line. But they are within the -4 to +4 standard deviation interval, so the experiments had no outliers. Therefore, it could be concluded that residuals are random and normally distributed.

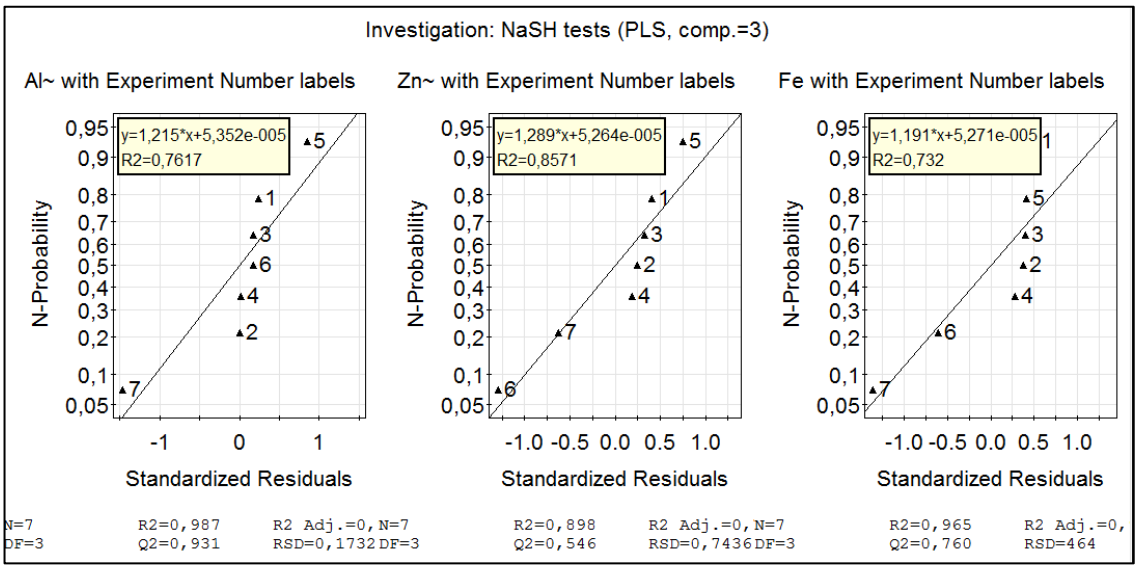


*Figure 19. Normal Probability Plot of standardized residuals of the sulfide precipitation model for Al, Zn, and Fe.*

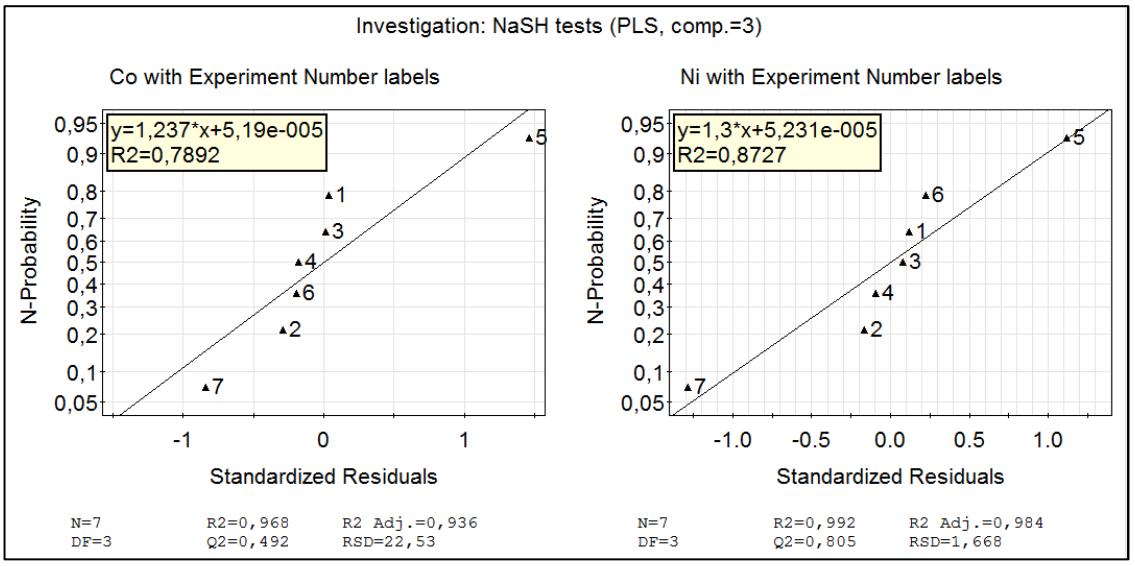


*Figure 20. Normal Probability Plot of standardized residuals of the sulfide precipitation model for Co and Ni.*

From Figure 21 and Figure 22 we could see Observed vs. Predicted Plot, which shows how close measured values of responses are to those predicted by the model. Since the developed model does not have high Q2 parameter, not all predicted values fall on the straight line. So the model does not predict the results of experiments well.

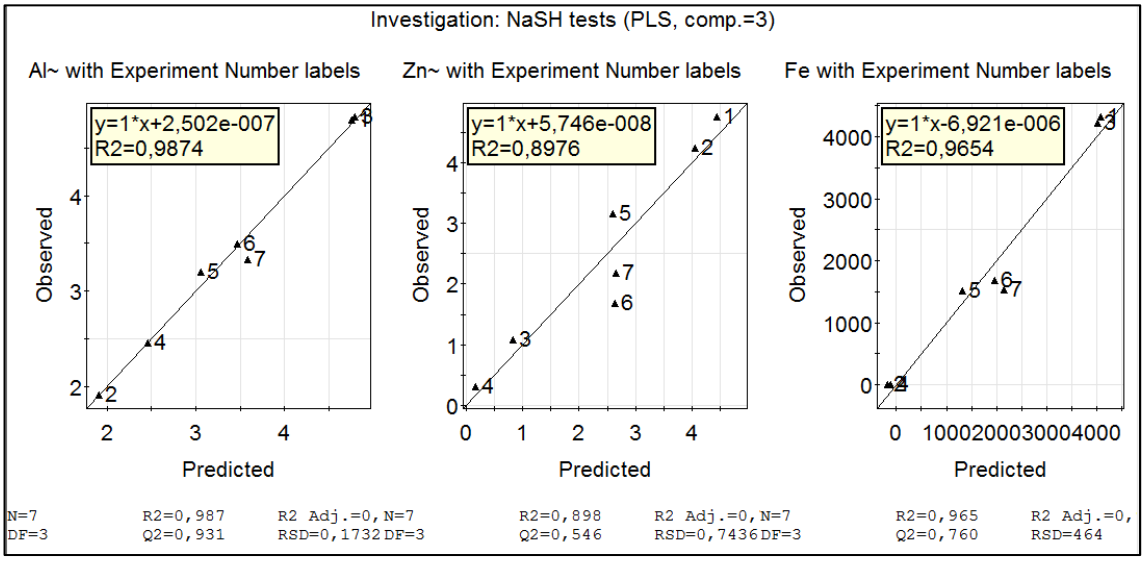


*Figure 21. Observed vs. Predicted Plot of the sulfide precipitation model for Al, Zn, and Fe.*

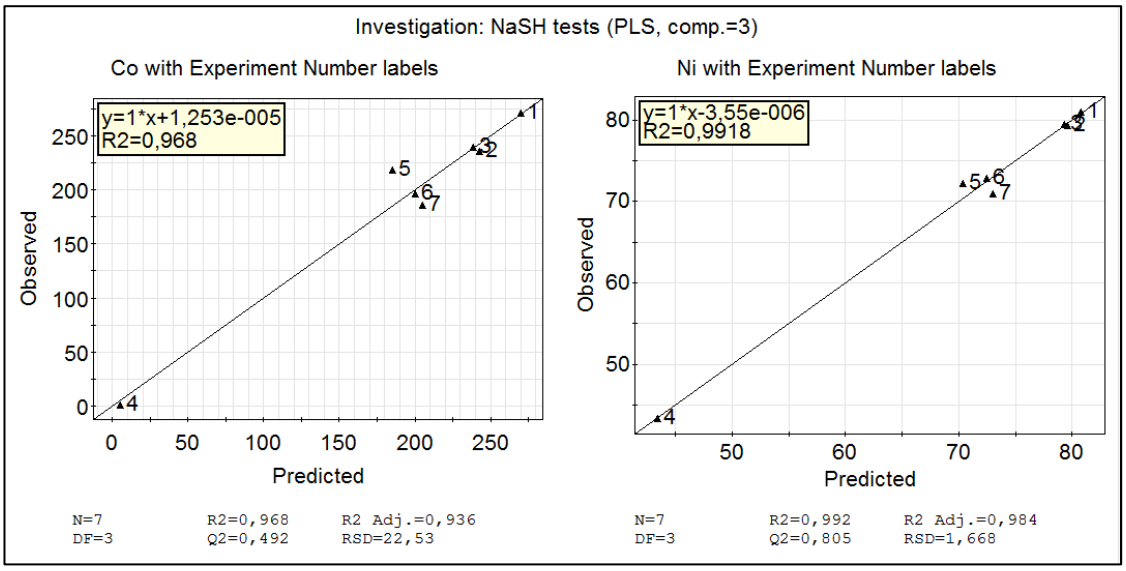


*Figure 22. Observed vs. Predicted Plot of the sulfide precipitation model for Co and Ni.*

Even though the designed model could not be said to be representative of the real system due to its poor predictive power (Q2) and validity, it is possible to use this model to illustrate correlation between all terms in the model and all the responses. Ten of the largest correlations are presented in Figure 23. What could be easily seen is high correlation between Co, Ni, and Zn concentrations after sulfide precipitation. However, it is important to remember that correlation does not imply causation. Cobalt and nickel have very similar properties and atomic weight, so they are likely to be removed by the same mechanisms and at the same pH range. Correlation between Al and Fe removal is also high, but this is due to the fact that both of them precipitate at low pH, which could also be seen from dependency of these metal residual content on pH during sulfide addition. What is also shown on this figure is inverse dependency of Zn, Co, and Ni concentrations on NaHS dose.

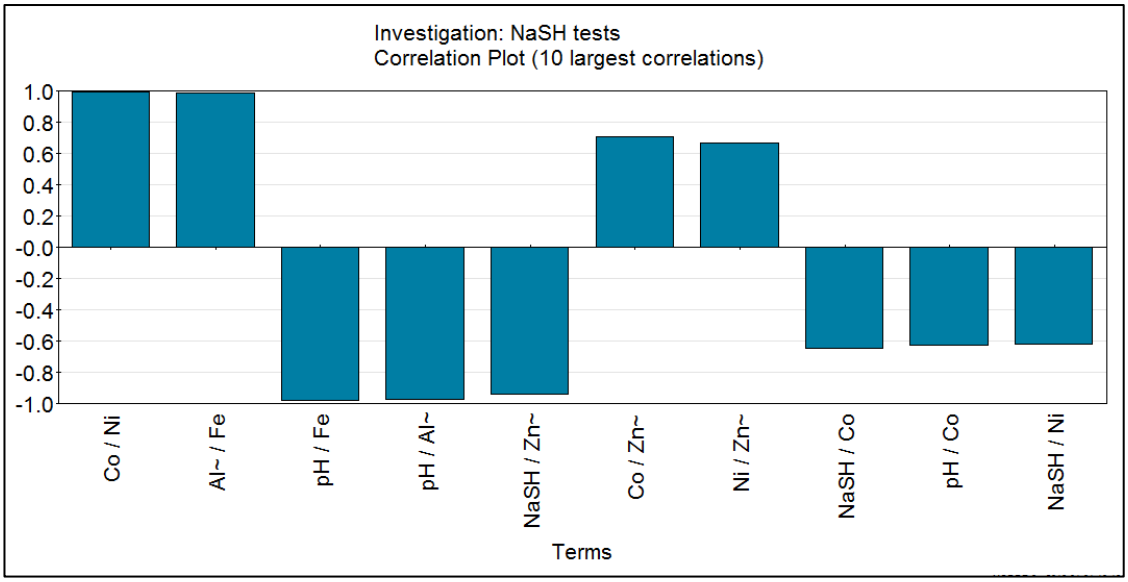


*Figure 23. Plot of 10 largest correlations of the sulfide precipitation model.*

## 6.2 Lime neutralization followed by Fenton reagent

Comprehensive results of analyses are presented in Appendix 7. Cells coloured in pink indicate values below the proposed discharge requirements.

In each of the seven experiments after Fenton treatment concentrations of Cd, Cr, Ni, Pb, and Zn were below those required by the proposed environmental targets. In all of the analysed samples concentrations of Cd were <0.05 µg/l, Pb <0.2 µg/l, and Zn <2 µg/l, which is below the limits of detection of ALS laboratory.

After lime treatment Cr, Ni, Pb, and Zn were already below the proposed discharge limits (see Table 18). Concentration of Zn was 20 times lower than what is typical Zn concentration in the treatment plant effluent. This signifies that it is possible to achieve better Zn removal using lime alone.

*Table 18. Results of polishing Fenton reagent treatment after lime neutralization.*

| Test No. | Fe dose, mg/l | pH | As, µg/l | Co, µg/l | Cr, µg/l | Cu, µg/l | Mn, µg/l | Ni, µg/l | Fe, µg/l | S, mg/l |
|---|---|---|---|---|---|---|---|---|---|---|
| Raw AMD | | 2.8 | 14.7 | 295.0 | 30.30 | 21900.0 | 4260 | 71.6 | 141.0 | 921 |
| After lime neutralization | | 9 | 0.9 | 0.2 | 1.72 | 4.2 | 122 | <0.5 | <4.0 | 921 |
| 1 | 30 | 9.5 | 0.5 | 0.7 | 0.791 | 1.5 | 2.5 | 0.8 | 26.2 | 948 |
| 2 | 100 | 9.3 | 0.5 | 0.6 | 1.63 | 1.1 | 1.4 | 1.0 | 48.5 | 958 |
| 3 | 65 | 9.5 | 0.6 | 0.2 | 1.34 | <1.0 | 1.3 | 1.6 | 31.3 | 960 |
| 4 | 65 | 9.3 | <0.5 | 0.1 | 0.932 | <1.0 | 1.3 | 1.0 | 47.1 | 984 |
| 5 | 65 | 9.3 | 0.8 | 0.3 | 0.754 | <1.0 | 0.5 | 1.4 | 23.0 | 1000 |
| 6 | 30 | 9.4 | <0.5 | 0.2 | 1.54 | <1.0 | 0.6 | 1.3 | 28.9 | 1020 |
| 7 | 100 | 9.3 | 0.5 | 0.1 | 1.22 | 1.2 | 0.8 | 1.0 | 33.5 | 980 |

The repeatability of experiments was quite poor, as results of centre point experiments were varying in a wide range. This could be attributed to difficulties in pH control and dosing of lime suspension, pipetting errors, contamination, mixing, measuring error, etc.

Compared to water quality after lime treatment, samples after Fenton reagent treatment had lower concentrations of all metals, except Fe, which was a secondary contaminant. Cadmium was successfully removed below the required limit and below the detection limit, while As and Cu concentrations in most cases were still higher than required. Since analysis of precipitate was not performed, it is not possible to say whether metals were removed due to adsorption on iron hydroxide, manganese hydroxide, or on lime particles.

## 6.3 Lime neutralization followed by Mn oxidation

Comprehensive results of analyses are presented in Appendix 7. Cells coloured in pink indicate values below the proposed discharge requirements.

For the main tests $H_2O_2$ was used as an oxidant. After $MnSO_4$ oxidation Magnafloc 10 (0.05%) was added to the solution to improve sedimentation. It was observed that most of the flocs were bonded together, though some small fines were still suspended. Moreover, in some cases the bonded flocs were rising to the surface some time after being precipitated on the bottom, as peroxide produced a lot of small bubbles. This should be considered when selecting flocculant and designing clarification and sludge removal systems. The results of experiments are presented in the Table 19 below. Cells coloured in pink indicate values below the proposed discharge requirements.

In each of the eight experiments after manganese oxidation treatment concentrations of Cd, Cr, Pb, and Zn were below those required by the proposed environmental targets. In all analysed samples concentrations of Zn were <2 µg/l, which is below the limits of detection of ALS laboratory.

*Table 19. Results of polishing treatment with $MnSO_4$ oxidation by $H_2O_2$ after lime neutralization.*

| Test No. | Mn dose, mg/l | pH | As, µg/l | Co, µg/l | Cr, µg/l | Cu, µg/l | Mn, µg/l | Ni, µg/l | Fe, µg/l | S, mg/l |
|---|---|---|---|---|---|---|---|---|---|---|
| Raw AMD | | 2.8 | 14.7 | 295.0 | 30.30 | 21900.0 | 4260 | 71.6 | 141.0 | 921 |
| After lime neutralization | | 9.3 | 0.90 | 0.19 | 2.24 | 3.9 | 63 | <0.5 | <4.0 | 914 |
| 1 | 50 | 9.7 | 0.60 | 0.09 | 1.96 | 2.1 | 15 | <0.5 | <4.0 | 970 |
| 2 | 200 | 9.3 | 0.60 | 0.08 | 1.94 | 1.1 | 109 | <0.5 | <4.0 | 962 |
| 3 | 125 | 9.1 | 0.75 | 0.11 | 1.65 | <1.0 | 5730 | <0.5 | <4.0 | 1010 |
| 4 | 125 | 8.9 | 0.54 | 0.32 | 1.59 | 1.2 | 44800 | <0.5 | <4.0 | 994 |
| 5 | 50 | 9 | 0.80 | 0.59 | 1.43 | <1.0 | 77000 | 1.0 | <4.0 | 1030 |
| 6 | 200 | 8.9 | 0.73 | 0.61 | 1.23 | <1.0 | 84100 | 0.6 | <4.0 | 1060 |
| 7 | 50 | 9.5 | 0.82 | <0.05 | 0.66 | <1.0 | 2970 | 0.6 | 4.3 | 921 |
| 8 | 125 | 9.4 | 0.66 | <0.05 | <0.50 | <1.0 | 27000 | <0.5 | <4.0 | 886 |

Results of $MnSO_4$ oxidation with $H_2O_2$ after lime treatment showed decrease in concentrations of all metals. However, removal of As was not significant and generally worse than that achieved by Fenton. Higher Mn concentration showed poor removal of As, Cd, Co, Ni, and Pb, while lower concentrations showed better results, except in case of Cu, when higher concentrations of Mn showed improved removal. Generally, compared to Fenton oxidation, 50 mg Mn/l was significantly superior at removing Co reaching levels below 0.1 µg/l, but was inferior otherwise. Moreover, at higher concentrations a lot of residual Mn was left in the solution. This could be due to insufficient reaction time and small particle size of $MnO_2$ precipitate that passed through a filter membrane. This would also explain higher residual metals concentrations at higher Mn dosages, as some $MnO_2$ particles could have had metal ions adsorbed on their surface.

Overall, the experiments showed that 50 mg Mn per litre neutralized AMD is a sufficient dose for polishing of lime treated mine water, as it helps to further decrease dissolved metal concentrations. Its treatment efficiency is comparable to that of Fenton and allows

reaching the proposed requirements for all the metals except As and Cu. The two experiments of $MnSO_4$ reaction with lime without addition of oxidant showed as good results as those of $MnSO_4$ with $H_2O_2$. However, the reaction was rather slow, and it was taking about 1 hour for big flocs to form. There also seemed to be less sludge, and it was initially not as dark brown as sludge formed in sample where $H_2O_2$ was added. However, removal of Co, Cr and Cu was higher than in case of oxidant addition, and residual Al was extremely low, below 5 µg/l. These could be due to the longer reaction time. But As removal was not as good as in experiments with oxidant, and residual Mn was quite high.

# 7 Discussion

The goal of the present thesis work was to find the best water treatment method for removal of metals from Kristineberg mine water and show whether or not they could satisfy environmental discharge requirements proposed by Boliden Mineral AB. The proposed requirements would impose discharge restrictions on the elements presented in the Table 20 below:

*Table 20. Kristineberg average incoming water quality for the year 2016 and proposed environmental discharge requirements.*

| Parameter (unfiltered sample) | Incoming water, µg/l | Proposed discharge requirements | |
|---|---|---|---|
| | | Monthly average, µg/l | Maximum allowed, µg/l |
| Al | 69350 | | |
| As | 35 | 0.5 | 8 |
| Cd | 173 | 0.25 | 1.5 |
| Cr | 31 | 3.4 | |
| Cu | 15381 | 0.5 | |
| Fe | 147433 | | |
| Hg | 0.03 | | 0.07 |
| Ni | 72 | 4 | 34 |
| Pb | 82 | 1.2 | 14 |
| U | 18 | | 8.6 |
| Zn | 74283 | 6 | |

The proposed requirements are considerably stricter than the current ones. It is a new tendency in Swedish environmental legislation to aim for analytical detection limit as a basis for discharge requirements, however, it is not always a justified approach that brings up several issues. Firstly, some metals are essential for aquatic ecosystems and should be present in water in small concentrations. For example, zinc is a vital microelement that is involved in nucleic acid synthesis and occurs in many enzymes [79]. When establishing the discharge limits several factors should be taken into account. It is important to remember that amount of bioavailable metals is not equal to total amount of metals present in water, as it depends on pH and temperature, water hardness, and presence of organic matter. Current discharge requirements for Kristineberg were made taking into the account bioavailability of Cd, Cu, and Zn. Another factor that has to be kept in mind is acute toxicity of metals, which could vary depending on presence of other pollutants. Background concentrations should also be considered when establishing discharge limits. If background concentrations of metals are naturally high ecosystems are adapted to these concentrations and any changes in water quality could shift the ecosystem balance [52]. Therefore, field observations on toxicity of water discharged to recipient are necessary to establish levels of metal concentrations harmless to aquatic life.

Secondly, as the present work showed, in laboratory conditions it was hard to achieve the new limits for all the metals at the same time even after using a two- and three-stage treatment methods and filtering final samples through 0.45 µm filter. Increasing number

of treatment stages would lead to significant increase in operational and investment costs. And scaling up processes from laboratory to full-scale usually results in at least 2 times higher residual concentrations. Therefore, it is hard to expect that these low values are practically achievable for a full-scale water treatment plant.

Thirdly, high investments are required from companies to change their existing water treatment operations, and in case of new projects it could deem them unfeasible due to high water treatment costs.

Fourthly, because these values are on the lower border of detection limit of analytical equipment, they are very hard to measure accurately, and the measuring error could be as high as 30-50%. This makes enforcement of these limits hard to control. And such inaccuracy could make a difference between paying and not paying environmental fines.

To sum up, the new limits do not necessarily lead to environmental benefits, are extremely hard to reach, require high investments, and make compliance very hard to control.

The current treatment plant at Kristineberg is based on HDS process, which utilizes lime for neutralization and precipitation of metals as hydroxides. Concentrations of Cr, Ni, Pb, Hg, and U in the effluent from the existing plant are consistently lower than demanded by the proposed discharge limits. However, concentrations of As and Cd are several times higher than the new limits, while concentrations of Zn and Cu are 10-fold and 30- fold higher, respectively. The produced sludge has high volume, low solids content, and is problematic to transport and dispose. In case of increase of mine production increase of mine drainage volume is expected, which would render existing treatment plant incapable to cope with high load and produce treated water of the required quality.

Overall, none of the commercial technologies reviewed in this work have shown that it is possible to reach effluent concentrations of all metals lower than the proposed requirements for Kristineberg. The best reference found was MetClean$^{TM}$ pilot plant with two Mn process columns combined with sulfide post-precipitation for treatment of flue gas wash water. The plant inlet flow was 5 $m^3$/h and it was installed after neutralization and clarification. Effluent metal concentrations after sulfide precipitation were below 10 µg/l, though Zn concentration was over 100 µg/l (see Section 2.3 Commercial methods).

Most of the academic research papers reviewed here were focusing on removal of metals from more heavily contaminated streams to values below 1 mg/l, and none of them have shown metals removal to levels below 1 µg/l. One of the mayor difficulties being mentioned was solid-liquid separation. Moreover, most of the research papers focus on removal of one or few metals, and rarely more than four, because removing all the metals in one process is usually not possible. All metals have different properties, require special reaction time, pH and reagents for precipitation.

Therefore, it could be concluded that the proposed discharge limits are unrealistically low, especially for As, and it is likely that a full-scale water treatment plant would not be able to consistently reach these limits for all the specified metals.

# 8 Recommendations

The following recommendation are based on field visits to the Kristineberg water treatment plant, literature review, and experimental work described in this thesis. The recommendations are divided into three categories: optimization of the existing treatment plant, addition of a polishing treatment step to the existing plant, and construction of a new plant to treat larger volumes of AMD if Kristineberg is expanded. These recommendations could also be applied to water treatment plants of other mines.

## *8.1 Optimization of the existing plant*

The results of laboratory experiments conducted in the present thesis work show that with lime neutralization much lower values of Cu and Zn could be achieved. Concentrations of Cu and Zn in main tests samples after lime treatment were below 5 µg/l. Assuming engineering design factor of 2, we could expect that a full-scale plant could reach 10 µg/l concentrations of Cu and Zn. Therefore, it could be suggested that the performance of existing plant should be optimized in order to improve metals removal efficiency. The main issues identified are lime slaking process, clarification, and sludge dewatering.

**Lime slaking**

Lime slaking temperature in the mixing tank should be above 60 °C in order to produce small hydrated lime particles with large reactive surface area. The process should be controlled by measuring temperature of the lime slurry and adjusting quicklime to water ratio [80]. Currently the ratio is fixed and temperature in the slaker is not constant. Increasing slaking temperature should make lime slurry more reactive, hence decreasing required lime consumption and improving metals precipitation.

**Clarification and dewatering**

Overflow of suspended solids from the thickener and poor quality of sludge after drum filter are currently a big issue. Surface load of the thickener is high, and often high sludge level in the thickener results in increased suspended solids concentration in the effluent. Average sludge level in the thickener is 4.2 m, which means that sludge accounts for 84% of the thickener's volume, while optimum level would be 30%. The bottleneck seems to be capacity of drum filter, which could not dewater more sludge than it currently does. To improve sludge dewatering possibility to install pressure filter, tube press filter, or centrifuge instead of the drum filter should be researched. Decreasing sludge level would increase clarification time, so suspended solids would have more time to settle and effluent would have better quality.

To avoid suspended particles in the effluent an Actiflo® plant could be installed instead of the existing thickener. Actiflo® is a compact coagulation, flocculation and sedimentation system with very low footprint. Compact design and low residence time allows for fast process adjustment. It has already been tested at Kristineberg and showed good results.

## 8.2 Construction of polishing treatment plant

The polishing treatment technologies discussed in this work, namely Fenton reagent and manganese oxidation, could help to further decrease the dissolved metal concentrations in the effluent water from the existing plant. Since Fenton reagent plants are already operating at other Boliden's sites, it would be a better choice. The experiments conducted during this work showed applying Fenton after neutralization allows to further decrease concentrations of all metals below the proposed limits, however, As and Cu concentrations were not consistently lower than required. It could be expected that on a large scale long retention and sedimentation time would lead to improved metals removal.

The experiments showed that more than stoichiometric addition of peroxide is required for successful operation of Fenton reagent, and that 65 mg Fe per litre of neutralized AMD is a sufficient dose. Bench-scale tests are recommended to further investigate the operational conditions and reagent doses required for the optimal metals removal.

## 8.3 Additional research into sulfide precipitation

The main advantage of sulfide precipitation over neutralization is that it produces sludge that could be sent to smelters. Large volumes of sludge are always problematic and create costs of transportation and disposing. Using sulfide precipitation amount of hydroxide sludge could be decreased, therefore decreasing the sludge handling costs. Hence it is a promising technology and its potential application should be researched further.

Laboratory experiments showed superior removal of Cu and Zn with sulfide precipitation compared to neutralization and polishing. Three-stage sulfide precipitation experiments showed that all elements except nickel could be removed to meet the proposed requirements. Additional tests are recommended to find optimum conditions for NiS removal. It is possible that nickel would be removed if during sulfide addition pH>10 is achieved. Using hydrogen sulfide gas as a sulfide source is also recommended. Combination of $N_2/H_2S$ would improve sulfide distribution, prevent supersaturation and formation of small fines, and remove oxygen from the solution. It is also recommended to make experiments with larger amounts of water to determine amount of sludge formed during precipitation, its composition, and suitability for processing at concentrator. Data from MetClean™ pilot plant combined with sulfide precipitation, reported in Section 2.3 Commercial methods, shows that effluent values of Ni below 7 µg/l are achievable [48].

It could be also recommended to use commercially developed technologies for pilot-tests of sulfide precipitation. One option could be ChemSulphide® process offered by BioteQ Environmental Technologies, which is based on metal sulfide precipitation with NaHS. Another option is SULFATEQ™ technology offered by Paques. It is based on biological process, simultaneously removes sulfate and produces sulfide for metals precipitation. There currently are some obstacles that prevent successful operation of biological sulfide plants in northern climate and additional research is needed to resolve them.

Based on the results of laboratory experiments, modelling, and literature review, a water treatment process scheme is proposed for combined removal of Cu and Zn sulfides after Fe and Al precipitation. Bench-scale tests are recommended to determine process parameters, lowest effluent concentrations achievable, and sludge quality.

The Figure 24 below shows a proposed scheme for separate removal of Fe and Al as hydroxides with subsequent recovery of Zn and Cu as sulfides. Water from the mine should first be collected in sedimentation ponds, where most of the ferric iron would precipitate and adsorb As, Cr, and Pb. The ponds are required for extreme rain events and in case treatment plant is out of operation. After sedimentation water enters high density sludge process for Fe and Al removal. There are two mixing tanks for pH adjustment with limestone and a lamella or conventional thickener for sedimentation and clarification. In the first mixing tank incoming water mixes with recirculated sludge from a clarifier to reach pH ca 3.5, and dry limestone is added to the second tank to further increase pH to ca 5.5. Lower pH would results in higher Fe and Al concentration in sulfide sludge. Increasing pH above 6 would results in less impurities in the sulfide sludge but loss of Cu content, as ca 80% of Cu is removed with Fe and Al at pH 6. Step-wise pH increase is recommended to avoid pH overshoot, increase reaction time and avoid formation of small fines. Sludge recirculation would decrease reagent consumption and improve floc formation. Using limestone would eliminate costs required for lime slaking. Moreover, limestone is the cheapest neutralization agent available. Using dry reagent decreases volume of water needed to be treated. And due to its properties it would not be possible to overshoot pH over 7. It is also known that limestone produces smaller volumes of sludge compared to slaked lime.

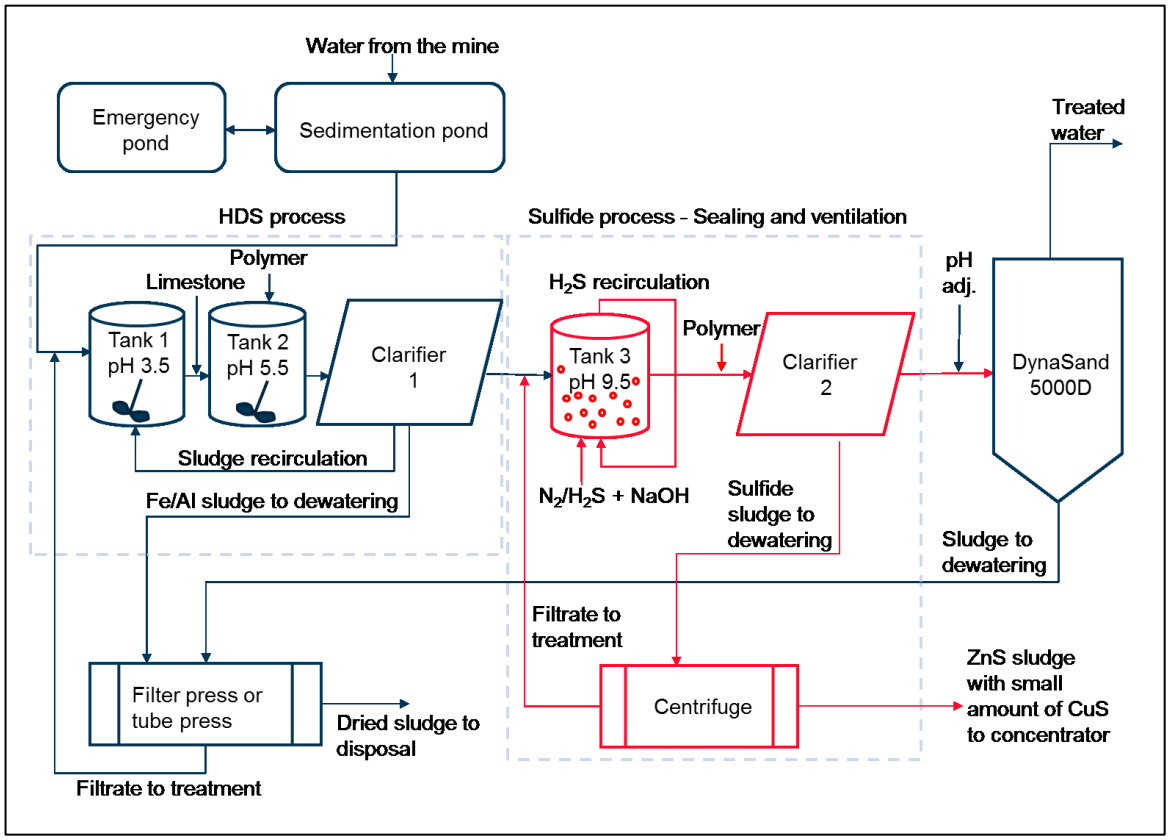


*Figure 24. Proposed process scheme for a new mine water treatment plant.*

The neutralized water could be settled in lamella clarifier with polymer addition. Using lamella would decrease footprint of the plant, however, sludge from conventional thickener is denser, and hence requires smaller sludge dewatering equipment. For dewatering the underflow from clarifier pressure filter could be used. Some part of underflow from thickener could be used for mine backfilling if needed. Filtrate should then be directed to

the first mixing tank and dewatered sludge could be utilized for mine backfilling. The overflow from the first clarifier enters the second mixing tank where it is mixed with a sulfide source and NaOH for pH control. Mixture of nitrogen and hydrogen sulfide gas could be used. Using gaseous sulfide addition is advantageous compared to liquid reagents, as it allows more even distribution of sulfide through the tank volume. Nitrogen acts as a carrier gas and simultaneously purges solution from oxygen, preventing oxidation of metals. For pH control use of sodium hydroxide is advice. It is a more expensive alkali agent but it would produce more pure sulfide sludge compared to lime addition. And because sodium hydroxide is readily soluble in water, it is more easily dosed and distributed through the solution volume. Special pS electrode should be used to automate control of sulfide dosage and avoid under- and overdosing. Underdosing would result in dissolved metals being left in the solution, hence poor removal efficiency. Overdosing is dangerous because excess sulfide causes formation of small particles that are hard to separate from solution, it could also cause precipitate to redissolve. Moreover, polysulfide species could form that consume sulfide and prevent it from reacting with metals. Lastly, excess of sulfide in solution could result in formation of thiosalts in the effluent. Therefore, it is important to keep stoichiometric sulfide addition.

After mixing sulfide sludge polymer should be added to improve clarification, and flocs should be separated in the second lamella or radial clarifier and then dewatered in a centrifuge. The sulfide precipitation equipment should be sealed and proper ventilation should be installed to avoid $H_2S$ leakages. Captured gas could be led to the third precipitation tank and reused. Clear water from the third sedimentation tank could be filtered through a sand filter or ultrafiltration membrane filter to ensure removal of all suspended particles. DynaSand$^{TM}$ filter is a continuously operating self-cleaning filter that does not require time for backwashing, so it could be a good choice. One DynaSand$^{TM}$ filter with 5 m diameter is required for 25 $m^3$/h flow, so several filters would be needed. The small amounts of sludge from sand filter could be mixed with hydroxide precipitation sludge and dewatered together.

In case bench-scale tests show that sand filter is not enough to capture small sulfide particles that don't settle in the clarifier, ultrafiltration filter could be installed instead. Pore size of UF filters ranges from 5 to 0.1 μm, so it could filter out colloidal matter, but does not need high pressure for operation. In this case reject water could be sent back to the beginning of sulfide process.

All equipment belonging to the sulfide precipitation stage should be sealed and have necessary ventilation to avoid presence of hydrogen sulfide gas in the water treatment plant building. In case there is large amount of sulfide gas coming from the third mixing tank, it could be captured and recirculated back to the process. Otherwise all gas should be collected and treated in scrubbers with, for example, sodium hydroxide.

The proposed plant should be able to reduce metal concentrations below the proposed limits, produce less gypsum sludge than currently used HDS plant, and recover most of the zinc from water together with small amount of copper.

# Reference list


[1] MEND Treatment Committee, "Study on metals recovery/recycling from acid mine drainage," *J. Chem. Inf. Model.*, vol. 53, no. July, pp. 1689–1699, 2013.

[2] Boliden AB, "The Boliden Area - Boliden." [Online]. Available: http://www.boliden.com/operations/mines/boliden-area/. [Accessed: 13-Sep-2017].

[3] Boliden AB, "Mineral Reserves and Mineral Resources 2016." [Online]. Available: https://www.boliden.com/sv/verksamhet/prospektering/mineralreserver-och-mineraltillgangar/. [Accessed: 03-Oct-2017].

[4] E. Carlsson, "Sulphide-Rich Tailings Remediated by Soil Cover," *Lulea Univ. Technol.*, pp. 1402–1544, 2002.

[5] J. Taylor, S. Pape, and N. Murphy, "A Summary of Passive and Active Treatment Technologies for Acid and Metalliferous Drainage (AMD)," *Proc. 5th Aust. Work. Acid Drain.*, no. 29, pp. 1–49, 2005.

[6] B. J. Baker and J. F. Banfield, "Microbial communities in acid mine drainage," *FEMS Microbiol. Ecol.*, vol. 44, no. 2, pp. 139–152, 2003.

[7] P. L. Hariani, S. Salni, and F. Riyanti, "Combination of CaCO3 and Ca(OH)2 as agents for treatment acid mine drainage," vol. 2004, pp. 2–6, 2017.

[8] A. E. Lewis, "Review of metal sulphide precipitation," *Hydrometallurgy*, vol. 104, no. 2, pp. 222–234, 2010.

[9] R. Peters, Y. Ku, and D. Bhattacharyya, "Evaluation of recent treatment techniques for removal of heavy metals from industrial wastewaters," *AICHE Symp. Ser.*, vol. 81, pp. 165–203, 1985.

[10] A. Velasco, M. Ramirez, S. Hernandez, W. Schmidt, and S. Revah, "Pilot scale treatment of chromite ore processing residue using sodium sulfide in single reduction and coupled reduction/stabilization processes," *J. Hazard. Mater.*, vol. 207–208, pp. 97–102, 2012.

[11] M. Ye *et al.*, "Removal of metals from lead-zinc mine tailings using bioleaching and followed by sulfide precipitation," *Chemosphere*, vol. 185, pp. 1189–1196, 2017.

[12] Y. S. Jung, W. T. Lim, J. Y. Park, and Y. H. Kim, "Effect of pH on Fenton and Fenton-like oxidation," *Environ. Technol.*, vol. 30, no. 2, pp. 183–190, 2009.

[13] E. Neyens and J. Baeyens, "A review of classic Fenton's peroxidation as an advanced oxidation technique," *J. Hazard. Mater.*, vol. 98, no. 1–3, pp. 33–50, 2003.

[14] H. Dong, X. Guan, D. Wang, C. Li, X. Yang, and X. Dou, "A novel application of H2O2-Fe(II) process for arsenate removal from synthetic acid mine drainage (AMD) water," *Chemosphere*, vol. 85, no. 7, pp. 1115–1121, 2011.

[15] Y. Deng and J. D. Englehardt, "Treatment of landfill leachate by the Fenton process," *Water Res.*, vol. 40, no. 20, pp. 3683–3694, 2006.

[16] USP Technologies, "Fentons Reagent General Chemistry." [Online]. Available: http://www.h2o2.com/industrial/fentons-reagent.aspx?pid=143&name=General-Chemistry-of-Fenton-s-Reagent. [Accessed: 05-Feb-2018].

[17] A. Mahiroglu, E. Tarlan-Yel, and M. F. Sevimli, "Treatment of combined acid mine drainage (AMD)-Flotation circuit effluents from copper mine via Fenton's process," *J. Hazard. Mater.*, vol. 166, no. 2–3, pp. 782–787, 2009.

[18] J. A. Z. and J. J. R. P Bautista, A F Mohedano, J A Casas, "Review. An overview of the application of Fenton oxidation to industrial wastewaters treatment," *J. Chem. Technol. Biotechnol.*, vol. 83, pp. 1323–1338, 2008.

[19] G. Lee, J. M. Bigham, and G. Faure, "Removal of trace metals by coprecipitation with Fe, Al and Mn from natural waters contaminated with acid mine drainage in the Ducktown Mining District, Tennessee," *Appl. Geochemistry*, vol. 17, no. 5, pp.

569–581, 2002.
[20] J. Sánchez-España, I. Yusta, and M. Diez-Ercilla, “Schwertmannite and hydrobasaluminite: A re-evaluation of their solubility and control on the iron and aluminium concentration in acidic pit lakes,” *Appl. Geochemistry*, vol. 26, no. 9–10, pp. 1752–1774, 2011.
[21] J. H. Park, Y. S. Han, and J. S. Ahn, “Comparison of arsenic co-precipitation and adsorption by iron minerals and the mechanism of arsenic natural attenuation in a mine stream,” *Water Res.*, vol. 106, pp. 295–303, 2016.
[22] G. F. Lee, “Session IV Transport Mechanisms: Role of Hydrous Metal Oxides in the Transport of Heavy Metals in the Environment,” *Proc. of Symposium of Transport of Heavy Metals in the Environment, IN: Progress in Water Technology 17: 137-147*, 1975. [Online]. Available: http://www.gfredlee.com/hydox.html. [Accessed: 02-Jan-2018].
[23] Y. W. Kang and K.-Y. Hwang, “Effects of Reaction Conditions on the Oxidation Efficiency in the Fenton Process,” vol. 34, no. 10, pp. 2786–2790, 2000.
[24] P. V. Nidheesh and R. Gandhimathi, “Trends in electro-Fenton process for water and wastewater treatment: An overview,” *Desalination*, vol. 299, pp. 1–15, 2012.
[25] M. N. Chong, B. Jin, C. W. K. Chow, and C. Saint, “Recent developments in photocatalytic water treatment technology: A review,” *Water Res.*, vol. 44, no. 10, pp. 2997–3027, 2010.
[26] A. Babuponnusami and K. Muthukumar, “Degradation of Phenol in Aqueous Solution by Fenton, Sono-Fenton and Sono-photo-Fenton Methods,” *Clean - Soil, Air, Water*, vol. 39, no. 2, pp. 142–147, 2011.
[27] K. Rout, M. Mohapatra, B. K. Mohapatra, and S. Anand, “Pb(II), Cd(II) and Zn(II) adsorption on low grade manganese ore,” *Int. J. Eng. Sci. Technol.*, vol. 1, no. 1, pp. 106–122, 2009.
[28] N. Demirkiran, “Copper adsorption by natural manganese dioxide,” *Trans. Nonferrous Met. Soc. China (English Ed.*, vol. 25, no. 2, pp. 647–653, 2015.
[29] P. M. Kohl and S. J. Medlar, *Occurrence of manganese in drinking water and manganese control*. AWWA Research Foundation, United States. Environmental Protection Agency, 2006.
[30] H. L. C. Loven, “Iron and Manganese Removal by Oxidation,” 1978.
[31] A. H. Lundquist, “Chemical and biological removal of iron and manganese from drinking water,” Montana State University, 1999.
[32] S. Wilson, W. Farone, G. Leonard, J. Birnstingl, and A. Leombruni, “Catalyzed Persulfate: Advancing In Situ Chemical Oxidation (ISCO) Technology,” *2013 Regenes. Bioremediation Prod. San Clemente, CA*, pp. 1–16, 2013.
[33] J. Wang and S. Wang, “Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants,” *Chem. Eng. J.*, vol. 334, no. October 2017, pp. 1502–1517, 2017.
[34] L. W. Matzek and K. E. Carter, “Activated persulfate for organic chemical degradation: A review,” *Chemosphere*, vol. 151, pp. 178–188, 2016.
[35] US EPA, “Alternative Disinfectants and Oxidants Guidance Manual,” 1999.
[36] W. R. Knocke, J. E. Van Benschoten, M. Kearney, *et al.*, “Alternative Oxidants for the Removal of Soluble Iron and Manganese,” 1990.
[37] M. Wekesa, J. Uddin, and H. F. Sobhi, “An Insight Into Mn(II) Chemistry: a Study of Reaction Kinetics Under Alkaline Conditions,” *Int. J. Chem. Res.*, vol. 2, no. 4, pp. 34–37, 2011.
[38] M. Wahlström, T. Kaartinen, *et al.*, *Water Conscious Mining*. Nordic Council of Ministers 2017, 2017.

[39] M. Nodwell and D. Kratochvil, “Sulphide Precipitation and Ion Exchange Technologies to Treat Acid Mine Drainage,” *9th Int. Conf. Acid Rock Drain.*, no. May 2012, 2012.
[40] BQE Water, “Raglan Mine, Glencore Xstrata.” [Online]. Available: https://www.bqewater.com/wp-content/uploads/2014/11/BQE-csRaglan-Mar2017w.pdf.
[41] Paques, “SULFATEQ™ - PAQUES.” [Online]. Available: http://en.paques.nl/products/other/sulfateq. [Accessed: 05-Oct-2017].
[42] J. L. Huisman, G. Schouten, and C. Schultz, “Biologically produced sulphide for purification of process streams, effluent treatment and recovery of metals in the metal and mining industry,” *Hydrometallurgy*, vol. 83, no. 1–4, pp. 106–113, 2006.
[43] Paques, “THIOTEQ™Metal - PAQUES.” [Online]. Available: http://en.paques.nl/products/other/thioteqmetal. [Accessed: 05-Oct-2017].
[44] “Veolia Water Technologies | High rate clarification | ACTIFLO® / ACTIFLO® PACK.” [Online]. Available: http://technomaps.veoliawatertechnologies.com/actiflo/en/. [Accessed: 11-Dec-2017].
[45] M. Farzad, “Electrocoagulation for Mine Water Treatment: Myths & Truths.” [Online]. Available: https://www.bqewater.com/electrocoagulation-mine-water-treatment-myths-truths/. [Accessed: 12-Dec-2017].
[46] P2W, “Heavy Metals and Arsenic Treatment in Mining Wastewater | P2W.” [Online]. Available: http://www.p2w.co/heavy-metals-and-arsenic-removal/. [Accessed: 05-Oct-2017].
[47] WaterTectonics, “Mine Tailings. Montana, USA.” [Online]. Available: http://www.groundtruthtrekking.org/Issues/MetalsMining/MineTailings.html.
[48] T. C. Christensen and U. Richter, “Treatment of water with dissolved heavy metals.”
[49] Porex Filtration, “POREX® Tubular Membrane Filter™ Modules For Metal Contaminated Wastewater Treatment & Reclamation Background.” [Online]. Available: http://www.porexfiltration.com/espanol/downloads/metal-contaminated-wastewater-treatment/.
[50] Boliden, “Boliden Annual Report 2016,” 2016.
[51] P. Nason, “Field and Pilot-Scale Geochemical Investigations Into Using Sewage Sludge for Sulphidic Mine Waste Remediation,” Luleå University of Technology Department of Civil, Environmental and Natural Resources Engineering Division of Geosciences and Environmental Engineering, 2012.
[52] L. O. Höglund and et. a. Herbert, R., “MiMi - Performance Assessment Main Report. MiMi 2003:3,” 2004.
[53] “London Metal Exchange: Home.” [Online]. Available: https://www.lme.com/. [Accessed: 05-Feb-2018].
[54] B. Lindquist, “Vatenreningsanläggningar i Boliden Mineral.”
[55] Golder Associates Ltd., “Operation of the Kristineberg High Density Sludge Treatment Plant,” 1999.
[56] European Environmental Agency, “Natura 2000 Network Viewer.” [Online]. Available: http://natura2000.eea.europa.eu/. [Accessed: 06-Feb-2018].
[57] Water Information System Sweden, “VISS - Water Information System Sweden.” [Online]. Available: http://viss.lansstyrelsen.se/SearchResults.aspx?ViewType=0&q=Vormbäcken&s=Sök. [Accessed: 03-Oct-2017].
[58] Swedish Agency for Marine and Water Management, “Klassificering och miljökvalitetsnormer avseende ytvatten (HVMFS 2013:19) - Föreskrifter - Stöd i

miljöarbetet - Havs- och vattenmyndigheten." [Online]. Available: https://www.havochvatten.se/hav/vagledning--lagar/foreskrifter/register-vattenforvaltning/klassificering-och-miljokvalitetsnormer-avseende-ytvatten-hvmfs-201319.html. [Accessed: 12-Dec-2017].

[59] Swedish Agency for Marine and Water Management, *Miljögifter i vatten – klassificering av ytvattenstatus Vägledning för tillämpning av HVMFS 2013:19*. 2016.

[60] D. G. Karamanev, L. N. Nikolov, and V. Mamatarkova, "Rapid simultaneous quantitative deteminations of feric and ferrous ionsin drainage waters and similar solutions," *Miner. Eng.*, vol. 15, pp. 341–346, 2002.

[61] Eurowater, "Products: SILEX IB and IIB." [Online]. Available: https://www.eurowater.com/products/silex-eurex/silex_ii_b.aspx. [Accessed: 12-Dec-2017].

[62] J. Lindgren and M. Karlsson, "Technical Report WinSGW The WinSGW Program – A Powerful Tool for Equilibrium Calculations in Multi Component and Multi Phase Systems Technical Report WinSGW 2 . x – 2002."

[63] S. Carrero, R. Pérez-López, A. Fernandez-Martinez, P. Cruz-Hernández, C. Ayora, and A. Poulain, "The potential role of aluminium hydroxysulphates in the removal of contaminants in acid mine drainage," *Chem. Geol.*, vol. 417, pp. 414–423, 2015.

[64] J. G. Webster, P. J. Swedlund, and K. S. Webster, "Trace metal adsorption onto an acid mine drainage iron(III) oxy hydroxy sulfate," *Environ. Sci. Technol.*, vol. 32, no. 10, pp. 1361–1368, 1998.

[65] L. K. Wang, *Handbook of industrial and hazardous wastes treatment*. Marcel Dekker, Inc, 2004.

[66] R. Smith and A. Martell, *Critical Stability Constants. Volume 4: Inorganic Complexes*. Plenum Press, New York, 1976.

[67] IUPAC and Academic Software, "IUPAC Stability Constants Database." 2000.

[68] C. E. Martínez and M. B. McBride, "Cd, Cu, Pb, and Zn coprecipitates in Fe oxide formed at different pH: aging effects on metal solubility and extractability by citrate.," *Environ. Toxicol. Chem.*, vol. 20, no. 1, pp. 122–126, 2001.

[69] M. M. Marchioretto, H. Bruning, and W. Rulkens, "Heavy metals precipitation in sewage sludge," *Sep. Sci. Technol.*, vol. 40, no. 16, pp. 3393–3405, 2005.

[70] R. A. D. Pattrick *et al.*, "The structure of amorphous copper sulfide precipitates: An X-ray absorption study," *Geochim. Cosmochim. Acta*, vol. 61, no. 10, pp. 2023–2036, 1997.

[71] G. Esposito, A. Veeken, J. Weijma, and P. N. L. Lens, "Use of biogenic sulfide for ZnS precipitation," *Sep. Purif. Technol.*, vol. 51, no. 1, pp. 31–39, 2006.

[72] R. M. M. Sampaio, R. A. Timmers, Y. Xu, K. J. Keesman, and P. N. L. Lens, "Selective precipitation of Cu from Zn in a pS controlled continuously stirred tank reactor," *J. Hazard. Mater.*, vol. 165, no. 1–3, pp. 256–265, 2009.

[73] Utmetrics Sartorius Stedim Biotech, "Design of experiments (DOE)." [Online]. Available: https://umetrics.com/how-it-works/doe. [Accessed: 05-Jan-2018].

[74] L. Eriksson, E. Johansson, N. Kettaneh-Wold, C. C. Wikström, and S. Wold, *Design of Experiments: Principles and Applications*. .

[75] N. Karbanee, R. P. Van Hille, and A. E. Lewis, "Controlled nickel sulfide precipitation using gaseous hydrogen sulfide," *Ind. Eng. Chem. Res.*, vol. 47, no. 5, pp. 1596–1602, 2008.

[76] H. Tokuda, D. Kuchar, N. Mihara, M. Kubota, H. Matsuda, and T. Fukuta, "Study on reaction kinetics and selective precipitation of Cu, Zn, Ni and Sn with H2S in single-metal and multi-metal systems," *Chemosphere*, vol. 73, no. 9, pp. 1448–1452,

2008.
[77] A. Lewis and A. Swartbooi, “Factors affecting metal removal in mixed sulfide precipitation,” *Chem. Eng. Technol.*, vol. 29, no. 2, pp. 277–280, 2006.
[78] Utmetrics, “Design of Experiments (DOE) Pharma Applications Design of Experiments (DOE) – Pharma Applications.” 2004.
[79] J. S. Alabaster and R. S. Lloyd, *Water quality criteria for freshwater fish*. Food and Agriculture Organization of the United Nations, 1982.
[80] M. Hassibi, “An Overview of Lime Slaking and Factors That Affect the Process,” 1999.

# List of appendices

# Appendix 1. SolGasWater modelling results for metal hydroxides solubility.

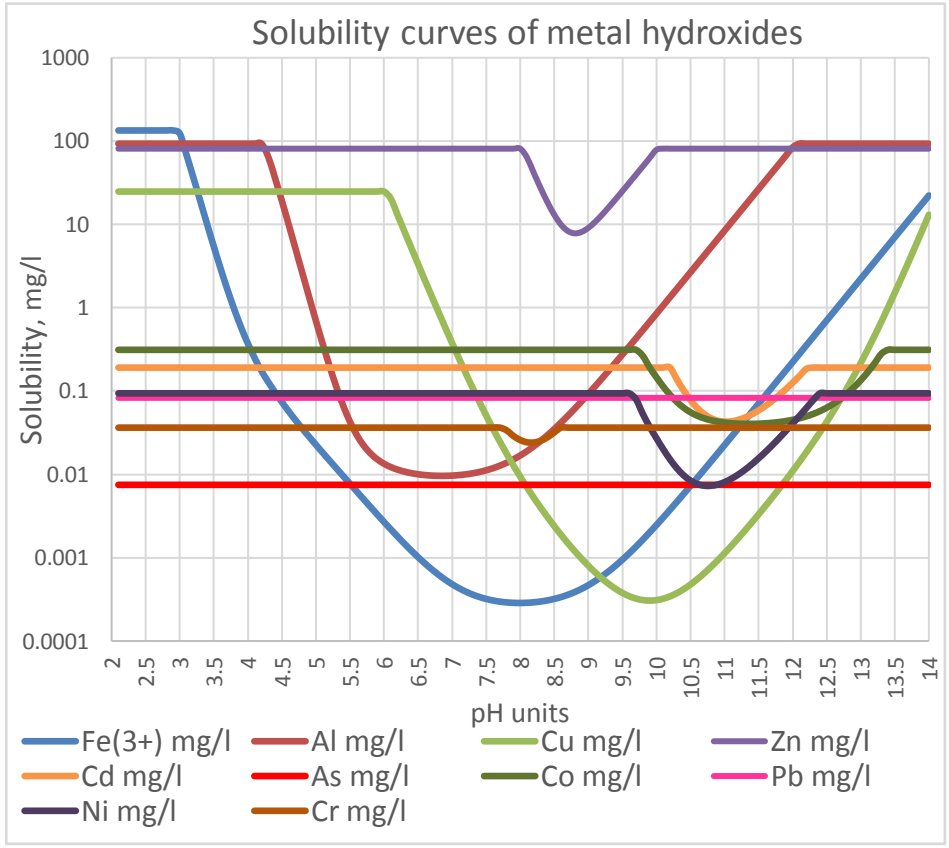


Figure 1. SolGasWater hydroxide precipitation model without ammonia.

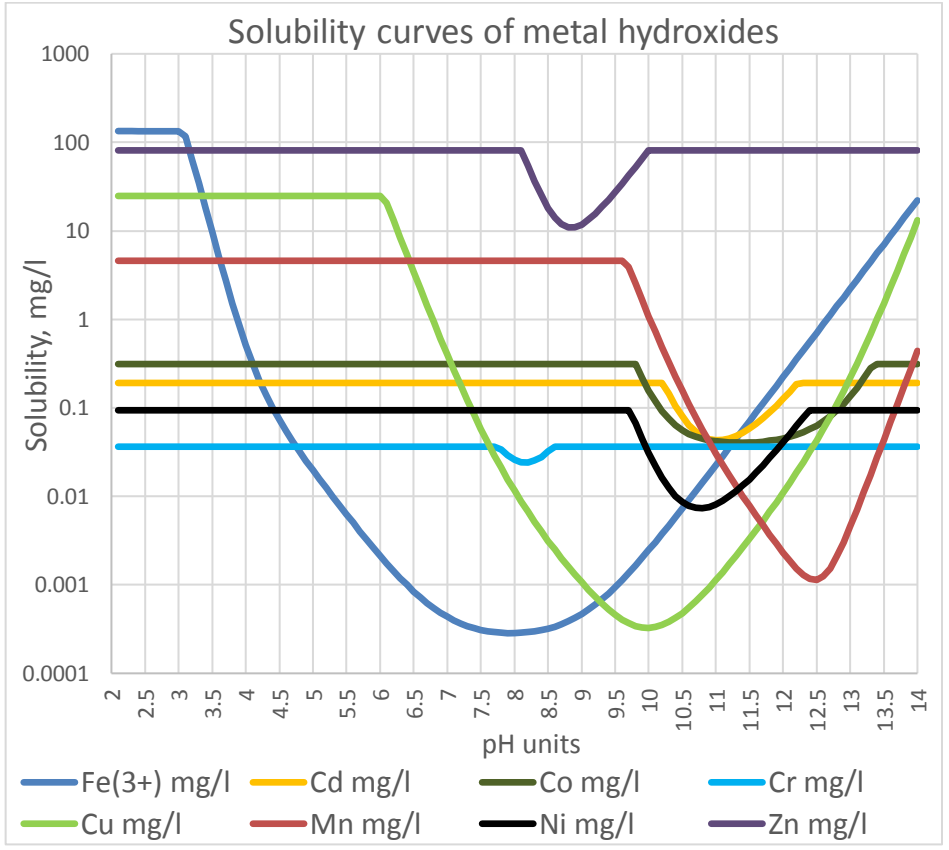


Figure 2. SolGasWater hydroxide precipitation model with ammonia.

## Appendix 2. SolGasWater modelling results for metal sulfides solubility.

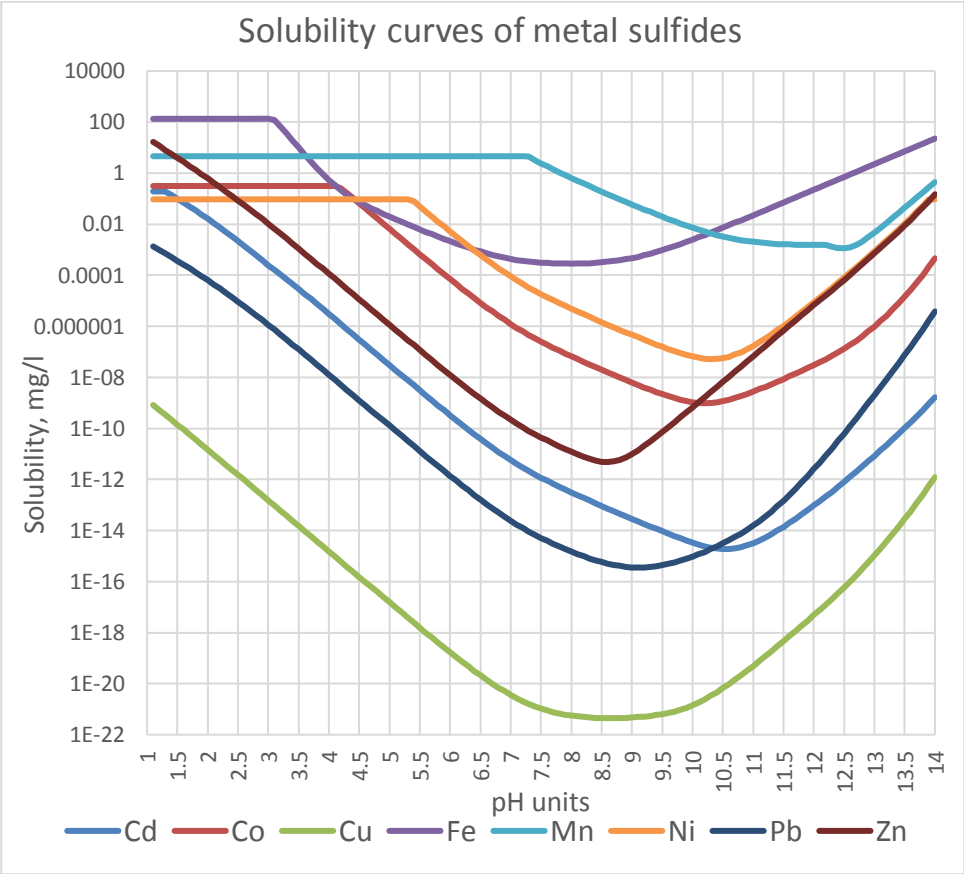


Figure 1. SolGasWater sulfide precipitation model Scenario 1 – stoichiometric sulfide addition.

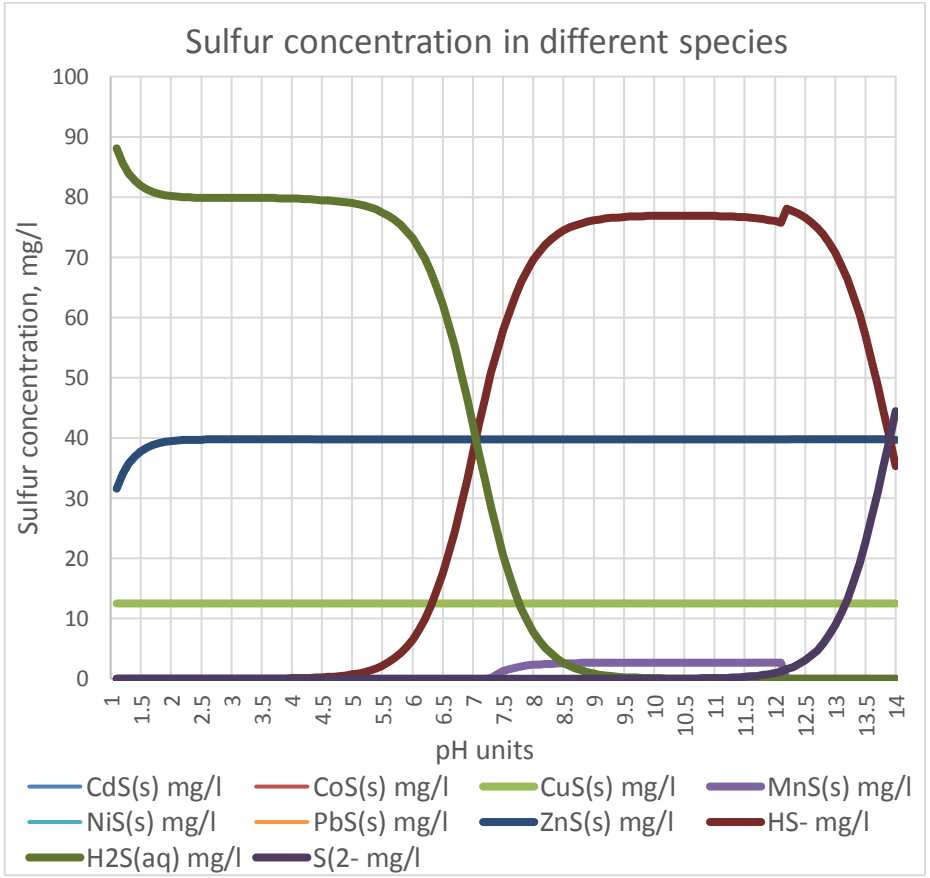


Figure 2. SolGasWater sulfide precipitation model Scenario 1 – stoichiometric sulfide addition.

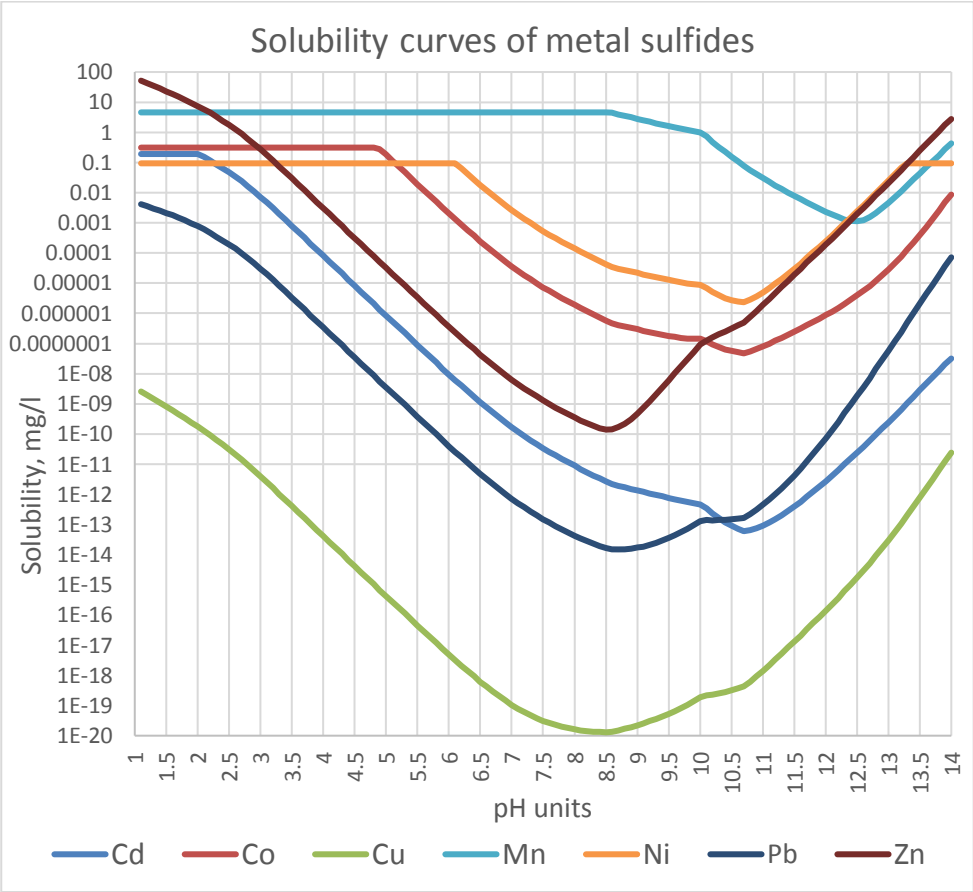


Figure 3. SolGasWater sulfide precipitation model Scenario 2 – stoichiometric sulfide addition after Fe precipitation.

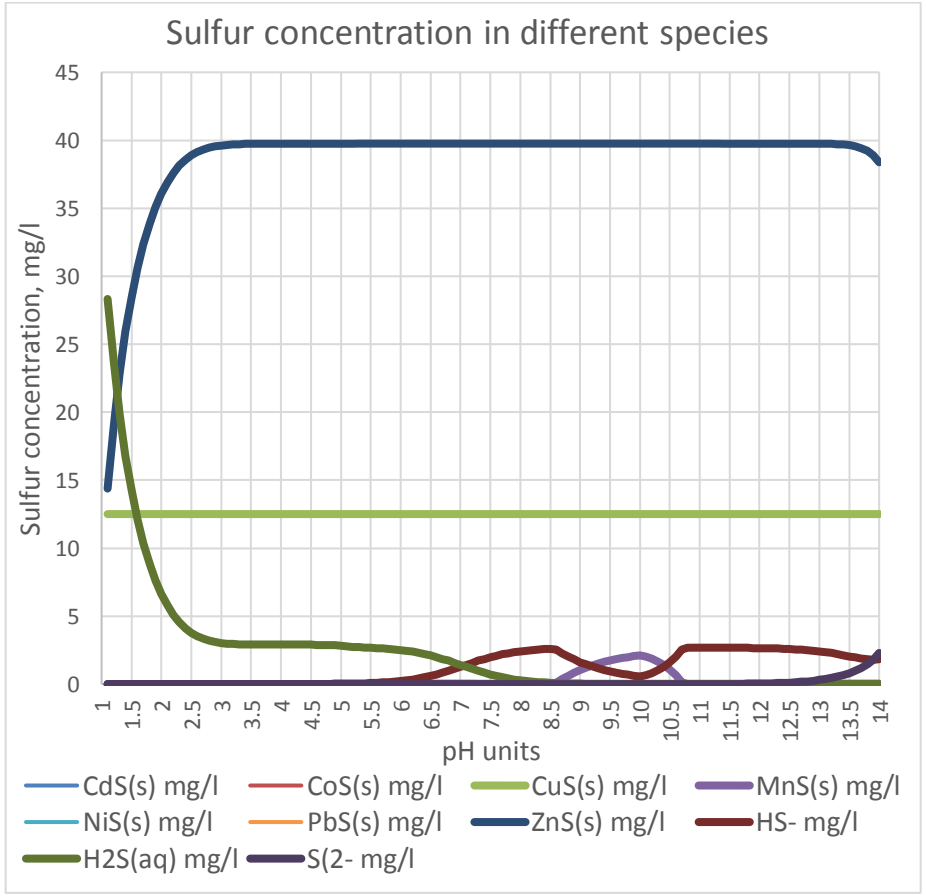


Figure 4. SolGasWater sulfide precipitation model Scenario 2 – stoichiometric sulfide addition after Fe precipitation.

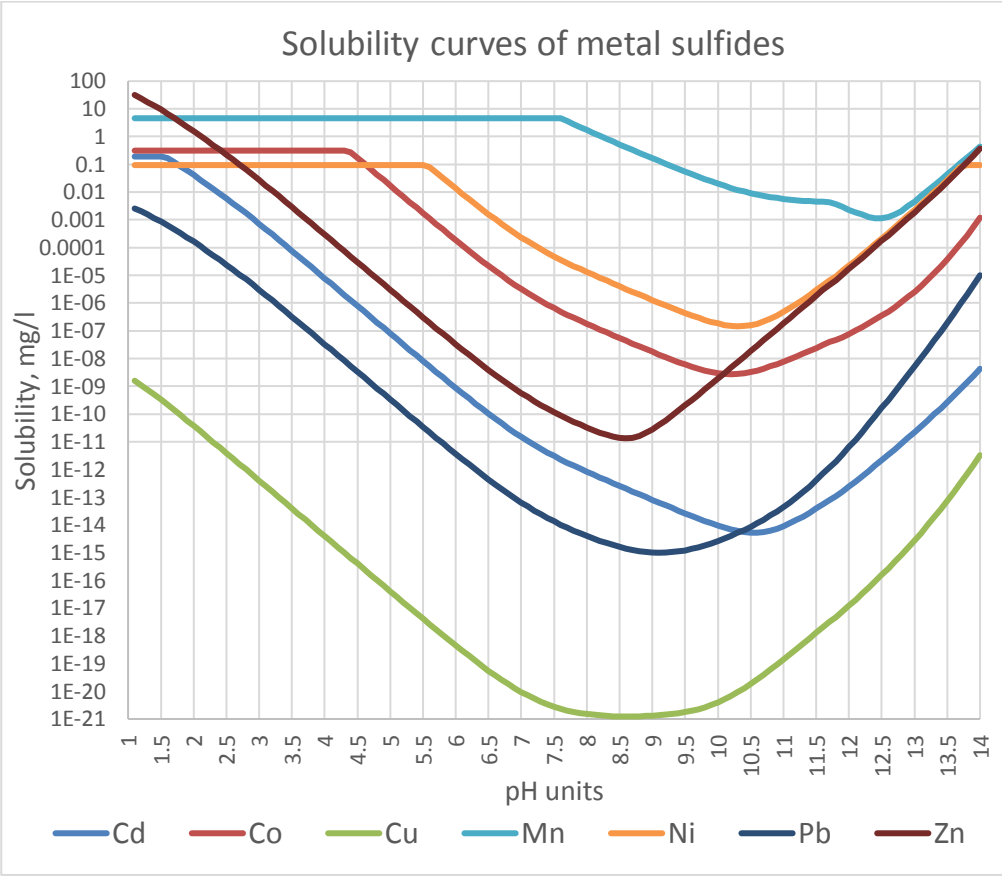


Figure 5. SolGasWater sulfide precipitation model Scenario 3- 1.5 times stoichiometric sulfide addition after Fe removal.

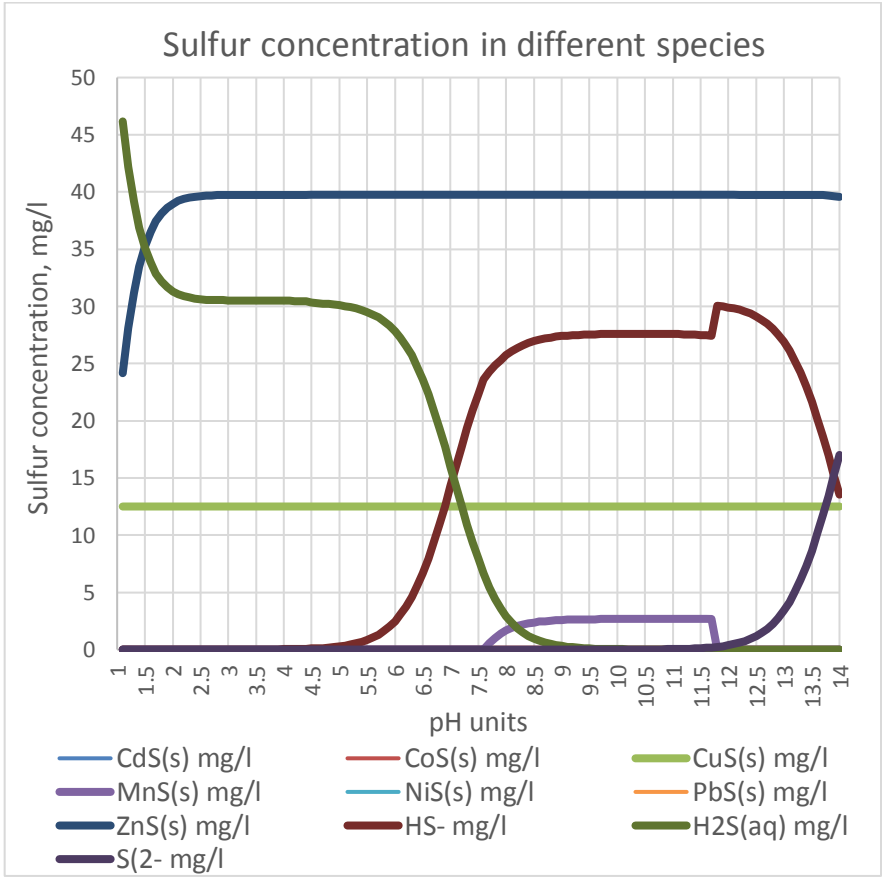


Figure 6. SolGasWater sulfide precipitation model Scenario 3 – 1.5 times stoichiometric sulfide addition after Fe removal.

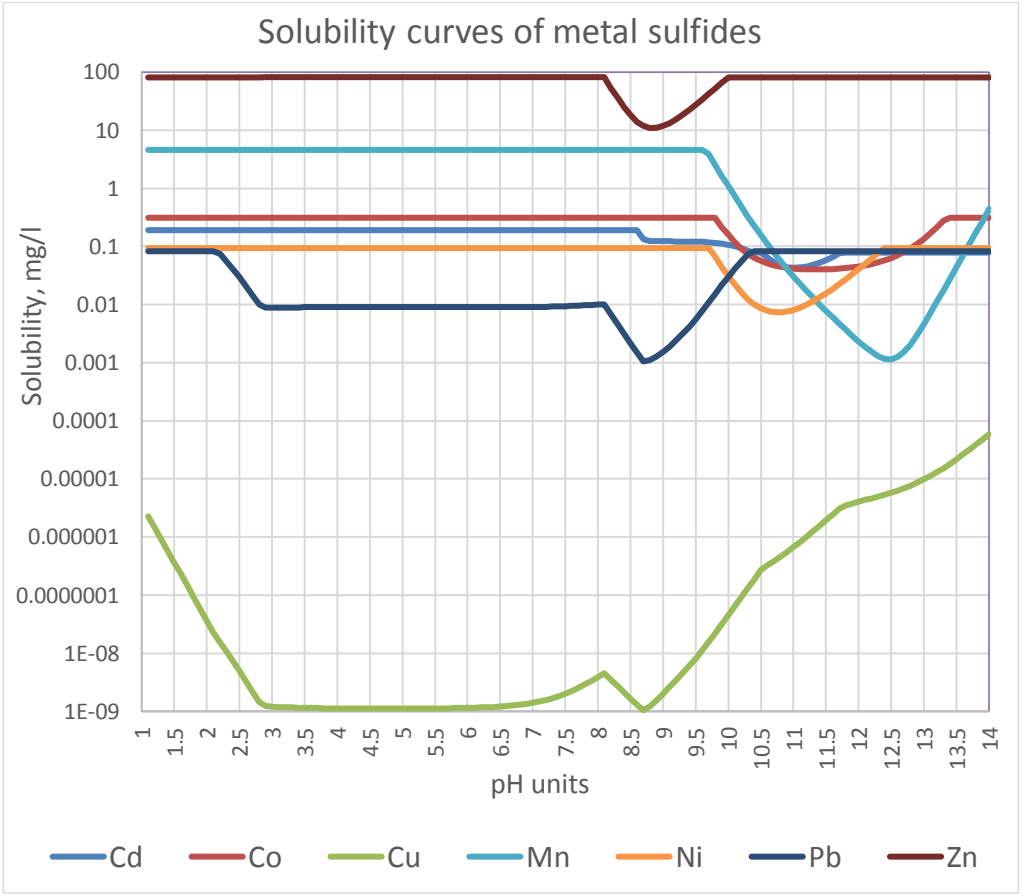


Figure 7. SolGasWater sulfide precipitation model Scenario 4 – after Fe removal, stoichiometric sulfide addition for selective Cu removal.

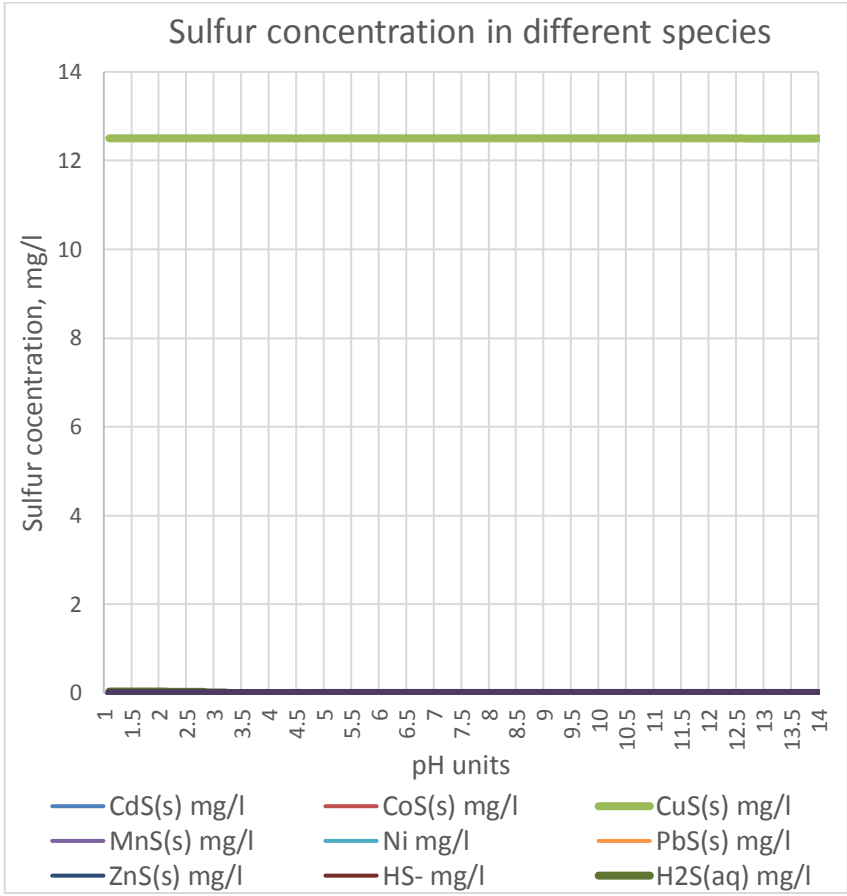


Figure 8. SolGasWater sulfide precipitation model Scenario 4 – after Fe removal, stoichiometric sulfide addition for selective Cu removal.

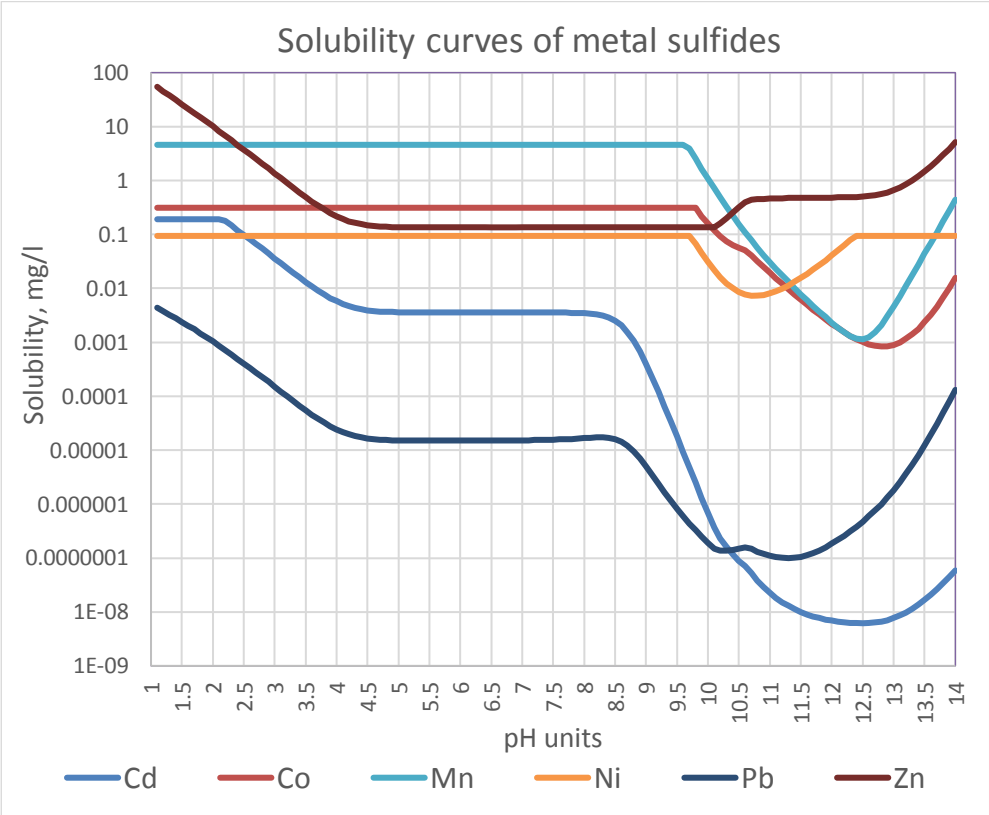


Figure 9. SolGasWater sulfide precipitation model Scenario 5 – after Fe and Cu removal, stoichiometric sulfide addition for selective Zn removal.

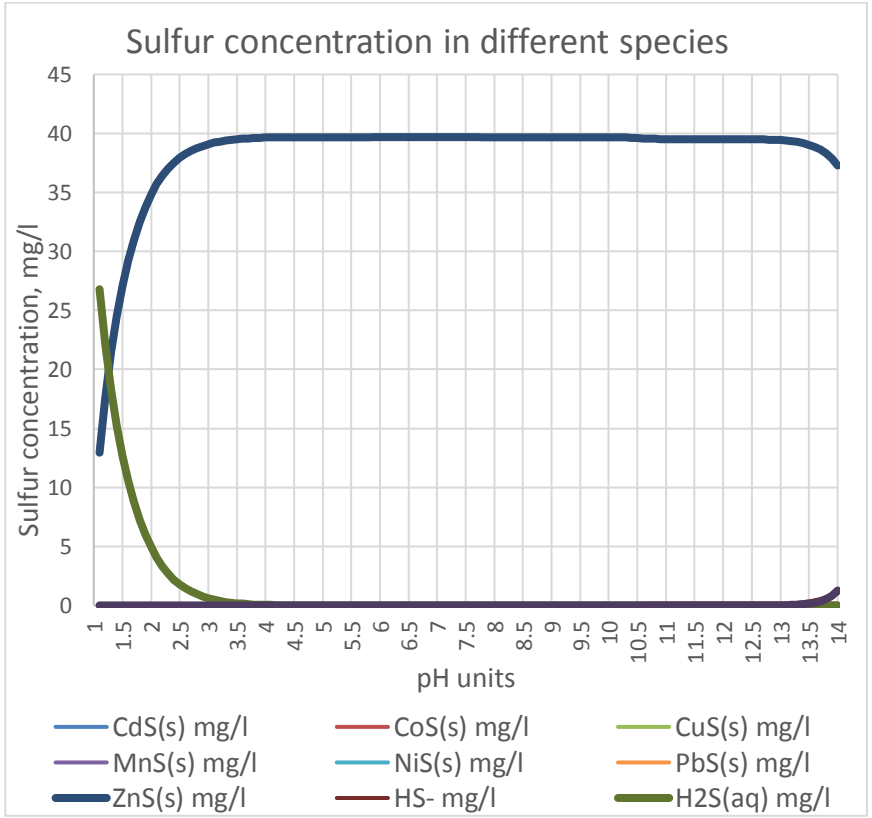


Figure 10. SolGasWater sulfide precipitation model Scenario 5 – after Fe removal, stoichiometric sulfide addition for selective Zn removal.

## Appendix 3. Metal hydroxides and sulfides solubility in comparison with the proposed requirements.

| Metal ion | Minimum hydroxide solubility, µg/l | Precipitation pH | Min. solub. pH | Minimum sulfide solubility, µg/l | Precipitation pH | Min. solub. pH | Monthly average treatment requirement, µg/l | Max. allowed concentration requirement, µg/l |
|---|---|---|---|---|---|---|---|---|
| $Al^{3+}$ | 9.61 | 4.3 | 6.9 | Does not form sulfides | | | | |
| $As^{2+}$ | Does not precipitate | | | | | | 0.5 | 8.0 |
| $Ca^{2+}$ | Does not precipitate | | | | | | | |
| $Cd^{2+}$ | 42.91 | 10.3 | 11 | $6.02*10^{-11}$ | 1.4 | 10.7 | 0.25 | 1.5 |
| $Co^{2+}$ | 40.38 | 9.8 | 11.3 | $9.66*10^{-7}$ | 4.2 | 10.2 | | |
| $Cr^{2+}$ | 24.12 | 7.8 | 8.2 | Does not form sulfides | | | 3.4 | |
| $Cu^{2+}$ | 0.31 | 6.1 | 9.9 | $4.45*10^{-19}$ | NA | 86 | 0.5 | |
| $Fe^{3+}$ | 0.29 | 3 | 8 | | | | | |
| $Mg^{2+}$ | 0.07 | 9.9 | 14 | | | | | |
| $Mn^{2+}$ | 1.14 | 9.7 | 12.5 | 1.14 $Mn(OH)_2$ | 7.3 MnS | 12.5 | | |
| $Ni^{2+}$ | 7.30 | 9.7 | 10.8 | $5.18*10^{-5}$ | 5.4 | 10.3 | 4.0 | 34.0 |
| $Pb^{2+}$ | Does not precipitate | | | $3.55*10^{-13}$ | NA | 9.1 | 1.2 | 14.0 |
| $Zn^{2+}$ | 10250.90 | 8.1 | 8.8 | $4.79*10^{-9}$ | NA | 8.6 | 6.0 | |

# Appendix 4. Results of ALS laboratory analysis of Kristineberg AMD

| Parameter | Units | Screening tests water, unfiltered, analysed 12.09.17 | Measuring uncertainty | Screening tests water, filtered, analysed 12.09.17 | Measuring uncertainty | Main tests water, filtered, analysed 28.11.17 | Measuring uncertainty |
|---|---|---|---|---|---|---|---|
| Ca | mg/l | 357 | ±34 | 355 | ±45 | 369 | ±46 |
| Fe | mg/l | 182 | ±22 | 134 | ±16 | 141 | ±17 |
| K | mg/l | 32.4 | ±2.8 | 32.2 | ±4.0 | 33.1 | ±4.1 |
| Mg | mg/l | 178 | ±21 | 177 | ±21 | 170 | ±20 |
| Na | mg/l | 57.9 | ±4.5 | 59.2 | ±7.3 | 70.7 | ±8.7 |
| Si | mg/l | 18.9 | ±2.9 | 17.9 | ±2.1 | 17.9 | ±2.1 |
| Al | µg/l | 94900 | ±13000 | 93400 | ±14400 | 84100 | ±13000 |
| As | µg/l | 20.6 | ±3.8 | 4.64 | ±0.84 | 14.7 | ±3.1 |
| Ba | µg/l | 43.1 | ±8.4 | 36.8 | ±7.2 | 25.1 | ±4.9 |
| Cd | µg/l | 191 | ±31 | 193 | ±25 | 176 | ±29 |
| Co | µg/l | 311 | ±48 | 315 | ±38 | 295 | ±38 |
| Cr | µg/l | 40.3 | ±7.7 | 36.1 | ±5.8 | 30.3 | ±6.2 |
| Cu | µg/l | 23400 | ±4250 | 25000 | ±3080 | 21900 | ±2680 |
| Hg | µg/l | 0.087 | ±0.0167 | 0.0359 | ±0.0188 | <0.02 | |
| Mn | µg/l | 4880 | ±840 | 4590 | ±541 | 4260 | ±501 |
| Mo | µg/l | <3 | | <1 | | 2.76 | ±0.92 |
| Ni | µg/l | 95.1 | ±19.1 | 91.1 | ±13.3 | 71.6 | ±14.6 |
| Pb | µg/l | 88.9 | ±17.0 | 86.3 | ±16.5 | 251 | ±48 |
| Sb | µg/l | 1.03 | ±0.31 | <0.2 | | 0.452 | ±0.124 |
| Sr | µg/l | 1110 | ±191 | 1030 | ±145 | 1150 | ±162 |

| Parameter | Units | Screening tests water, unfiltered, analysed 12.09.17 | Measuring uncertainty | Screening tests water, filtered, analysed 12.09.17 | Measuring uncertainty | Main tests water, filtered, analysed 28.11.17 | Measuring uncertainty |
|---|---|---|---|---|---|---|---|
| U | µg/l | 20.8 | ±4.0 | 22.9 | ±4.5 | 19.1 | ±3.8 |
| V | µg/l | 2.10 | ±0.66 | 0.102 | ±0.070 | 0.182 | ±0.152 |
| Zn | µg/l | 81600 | ±9430 | 81100 | ±9970 | 78000 | ±9410 |
| Stabilized with $H_2O_2$ for S analysis | | No | | Yes | | Yes | |
| S | mg/l | 953 | ±78 | 961 | ±148 | 921 | ±142 |
| $SO_4$ | mg/l | 2600 | ±390 | | | 2780 | ±418 |
| N tot | mg/l | 27.0 | ±8.11 | | | | |
| $NH_4$-N | mg/l | 11.0 | ±1.65 | | | | |
| $NO_3$-N | mg/l | 14.2 | | | | | |
| $NO_2$-N | mg/l | 0.764 | ±0.115 | | | | |

Unfiltered sample was analysed for total concentrations. The analysis was done after diluting 12ml samples with 1.2 ml ultrapure nitric acid and treating it in autoclave. ICP-SFMS (inductively coupled plasma sector field mass spectrometry) was used for determination of As, Cr, Cu, Mn, Pb, and U. ICP-AES was used for determination of Fe, S, Si, Al, Cd, Co, Ni, and Zn. Mercury was determined with atomic fluorescence spectrometry (AFS).

Filtered samples were analysed for dissolved metal concentrations, i.e. they were filtered through a 0.45 µm filter prior to being sent for analysis. These samples were not digested prior to analysis. ICP-SFMS (inductively coupled plasma sector field mass spectrometry) was used for determination of Fe, Al, As, Cd, Co, Cr, Cu, Pb, Ni, and U. ICP-AES was used for determination of S, Si, Mn, and Mg. Mercury was determined with atomic fluorescence spectrometry (AFS). Analysis with ICP-SFMS has been done according to SS EN ISO 17294-1, 2 (mod) and EPA method 200.8 (mod). Analysis with ICP-AES has been done according to SS EN ISO 11885 (Mod) and EPA Method 200.7 (Mod). Hg analysis with AFS has been done

according to SS EN ISO 17852. Sulfate content was measured according to CZ_SOP_D06_02_068 (CSN ISO 10304-1, CSN EN 16192) Determination of dissolved fluoride, chloride, nitrite, bromide, nitrate and sulfate by ionic liquid chromatography and determination of nitrite nitrogen and nitrate nitrogen and sulfate sulfur by calculation from measured values.

# Appendix 5. Results of screening tests. Analyzed by ICP-OES at Boliden's laboratory

Legend: pink cells – below requirement for a given metal, blue cells – conform to requirements for all metals.

| Test No. | No. of stages | Test name | Reagent dose, ml | pH | Al, µg/l | As, µg/l | Cd, µg/l | Co, µg/l | Cr, µg/l | Cu, µg/l | Mn, µg/l | Ni, µg/l | Pb, µg/l | Zn, µg/l | Fe, µg/l | Acid dilu-tion |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Raw water, unfiltered ALS results | 0 | 2.6 | 94900 | 20.6 | 191 | 311 | 40.3 | 23400 | 4880 | 95.1 | 88.9 | 81600 | 182000 | |
| | | Treated water quality at Kristineberg, av. for 2016 | | | 684 | 1.3 | 2.31 | 1.32 | 0.49 | 36.38 | 268.17 | 0.38 | 11.75 | 191.09 | 247.67 | |
| | | Requirements | | | | 0.5 | 0.25 | | 3.4 | 0.5 | | 4 | 1.2 | 6 | | |
| **Analysis done 26.10**. One-stage neutralization treatment. Solid reagents used, except in test 5.0 liquid 0.4M NaOH was used (analysed 24.11). | | | | | | | | | | | | | | | | |
| 5.0 | 1 | 200ml AMD+NaOH | 14.6 | 9.5 | 804 | 0 | 1 | 2.7 | 0 | 9.6 | 16.2 | 11.3 | 2.4 | 82.1 | 18.9 | yes |
| 1.1 | 1 | 200ml AMD+NaOH | 0.2275g | 9.2 | 1149 | 0 | 0 | 0.3 | 0 | 0 | 34.5 | 0 | 0 | 1.3 | 3.0 | |
| 1.2 | 1 | 200ml AMD+$Ca(OH)_2$ | 0.9557g | 9.4 | 139 | 0 | 0 | 1.6 | 0 | 0 | 0 | 0 | 0 | 0 | 3.7 | |
| 1.3 | 1 | 200ml AMD+$CaCO_3$ | 0.8832g | 6.2 | 112 | 0 | 97.2 | 285.1 | 0 | 1135.5 | 4090.3 | 68.8 | 0 | 52283.7 | 132.8 | |
| 1.4 | 1 | 200ml AMD+$Mg(OH)_2$ | 0.5848g | 6.7 | 62 | 0 | 128.8 | 271.2 | 0 | 50.6 | 4158.1 | 69.3 | 2.1 | 30099.6 | 2.7 | |
| **Analysis done 26.10.** Two-stage treatment: sulfide precipitation followed by glass fibre filtration and pH adjustment with sodium hydroxide. Reagent concentrations: $Na_2S$ 0.12M, NaHS 0.12M, TMT15® undiluted, NaOH 0.1M. | | | | | | | | | | | | | | | | |
| 2.2 | 1 | 200ml AMD + $Na_2S$ | 10 | 4.2 | 42398 | 18.7 | 0 | 0 | 3.8 | 0 | 3902.1 | 51.4 | 3.7 | 61.1 | 87125.4 | |
| 2.2 | 2 | 200ml AMD + $Na_2S$ + NaOH | 10+11 | 9.6 | 125 | 21 | 0 | 0 | 0 | 0 | 5 | 0 | 0 | 0 | 3958.3 | |
| | | | | | | | | | | | | | | | | |
| 2.3 | 1 | 200ml AMD + NaHS | 30 | 4.1 | 42287 | 0 | 0 | 38.2 | 13.9 | 0 | 3756.7 | 59.2 | 0 | 27.2 | 90782.0 | |
| 2.3 | 2 | 200ml AMD + NaHS + NaOH | 30+10.5 | 9.5 | 287 | 0 | 0 | 0 | 0 | 0 | 10.4 | 0 | 0 | 1.7 | 3109.0 | |

| Test No. | No. of stages | **Test name** | **Reagent dose, ml** | **pH** | **Al,** µg/l | **As,** µg/l | **Cd,** µg/l | **Co,** µg/l | **Cr,** µg/l | **Cu,** µg/l | **Mn,** µg/l | **Ni,** µg/l | **Pb,** µg/l | **Zn,** µg/l | **Fe,** µg/l | **Acid dilu-tion** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2.4 | 1 | 200ml AMD + TMT15® | 1.4 | 4.4 | 17648 | 8.5 | 0 | 135.9 | 0 | 0 | 4169.2 | 72.5 | 4.1 | 40331.4 | 85383.7 | |
| 2.4 | 2 | 200ml AMD + TMT15® + NaOH | 1.4+9.7 | 9.5 | 217 | 0 | 0 | 6 | 0 | 0 | 87.1 | 0 | 0 | 293 | 2486.9 | |
| | | | | | | | | | | | | | | | | |
| 2.5 | 1 | 200 ml AMD + TMT15® | 2 | 5.5 | 274 | 9.8 | 0 | 129 | 0 | 0 | 4006.7 | 44.2 | 0 | 4849.6 | 58140.5 | |
| 2.5 | 2 | 200 ml AMD + TMT15® + NaOH | 2+7.8 | 9.5 | 193 | 6.4 | 0 | 60.5 | 0 | 0 | 107.7 | 0 | 0 | 0 | 1140.1 | |
| **Analysis done 03.11**. Two-stage treatment: sulfide precipitation followed by glass fibre filtration and pH adjustment with calcium hydroxide. Reagent concentrations: NaHS 0.12M, $Ca(OH)_2$ 0.2M. Analysis of solution after NaHS addition was not done. | | | | | | | | | | | | | | | | |
| 3.2 | 2 | 200ml AMD + NaHS + $Ca(OH)_2$ | 20+6.5 | 4.5, 9.5 | 99 | 0 | 0 | 0 | 0 | 0 | 0 | 0.1 | 0 | 0 | | yes |
| **Analysis done 03.11**. Two-stage treatment: AMD neutralization with calcium hydroxide followed by glass fibre filtration, pH adjustment, Fenton reagent treatment, and final pH adjustment first to 9 and then to 10 (for Cd removal). Reagent concentrations: $FeSO_4$ 10g/l, $H_2O_2$ 3.3%, $Ca(OH)_2$ 0.2M. | | | | | | | | | | | | | | | | |
| 4.0 | 1 | 800ml AMD + $Ca(OH)_2$ | 60 | 9.3 | 2882 | 0 | 0.6 | 0 | 0 | 0.1 | 18.1 | 0 | 0 | 0.3 | | yes |
| | | | | | | | | | | | | | | | | |
| 4.1 | 2 | 200ml AMD + $FeSO_4$ + $H_2O_2$ | 0.5+0.2 | 3.6 | 2663 | 5.6 | 0.2 | 25.2 | 0 | 2.1 | 76.3 | 3.6 | 0 | 17.3 | | yes |
| 4.1a | | + $Ca(OH)_2$ | | 8.9 | 828 | 12.2 | 0 | 2 | 0 | 0 | 0.3 | 0 | 0 | 0 | | yes |
| 4.1b | | + $Ca(OH)_2$ | | 10.0 | 125 | 4.2 | 0 | 1.4 | 0 | 0 | 0 | 0 | 0 | 0 | | yes |
| | | | | | | | | | | | | | | | | |
| 4.2 | 2 | 200ml AMD + $FeSO_4$ + $H_2O_2$ | 1+0.4 | 4.0 | 2234 | 11.3 | 0.2 | 22.6 | 0 | 5.4 | 121.3 | 18.4 | 0 | 19.8 | | yes |
| 4.2a | | + $Ca(OH)_2$ | | 8.9 | 521 | 0 | 0 | 0 | 0 | 0 | 0 | 2.6 | 0 | 0 | | yes |
| 4.2b | | + $Ca(OH)_2$ | | 10 | 123 | 18.7 | 0 | 2.1 | 0 | 0 | 0 | 0 | 0 | 0 | | yes |

| Test No. | No. of stages | **Test name** | **Reagent dose, ml** | **pH** | **Al,** µg/l | **As,** µg/l | **Cd,** µg/l | **Co,** µg/l | **Cr,** µg/l | **Cu,** µg/l | **Mn,** µg/l | **Ni,** µg/l | **Pb,** µg/l | **Zn,** µg/l | **Fe,** µg/l | **Acid dilu-tion** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 4.3 | 2 | 200ml AMD + $FeSO_4$ + $H_2O_2$ | 2+0.8 | 4.2 | 3005 | 11.3 | 0.4 | 22.3 | 0 | 10.9 | 235 | 33 | 0 | 50 | | yes |
| 4.3a | | + $Ca(OH)_2$ | | 9.3 | 517 | 2.7 | 0 | 0.4 | 0 | 0 | 0 | 0 | 0 | 0 | | yes |
| 4.3b | | + $Ca(OH)_2$ | | 10.1 | 384 | 9 | 0 | 0 | 0 | 0 | 0 | 2.5 | 0 | 0 | | yes |
| **Analysis done 24.11.** Two-stage treatment: pH adjustment to ca 5 with sodium hydroxide followed by Fenton reagent treatment, pH adjustment to 8.6, $MnSO_4$ oxidation with peroxide, and final pH adjustment to 10. Reagent concentrations: $FeSO_4$ 10g/l, $H_2O_2$ 33%, $MnSO_4$ 10g/l, $Na_2S_2O_8$ 6%, NaOH 0.2M. | | | | | | | | | | | | | | | | |
| 5.1 | 1 | 200ml AMD + $FeSO_4$ + $H_2O_2$ | 3+0.2 | 5.2 | 2692 | 16.1 | 158.3 | 256.3 | 0 | 7574.1 | 4160.3 | 100.1 | 0.4 | 58563.9 | 29.8 | yes |
| 5.2 | 2 | + $MnSO_4$ + $Na_2S_2O_8$ | 3+1.5 | 8.6 | 77 | 5.1 | 13.1 | 27.1 | 0 | 10.3 | 11523.6 | 7 | 0 | 750.1 | 14.8 | yes |
| 5.3 | | +NaOH | | 10 | 68 | 0 | 0 | 6.9 | 0 | 5.1 | 0.7 | 1.2 | 0 | 19 | 17 | yes |
| | | | | | | | | | | | | | | | | |
| 5.7 | 1 | 200ml AMD+$FeSO_4$+$H_2O_2$ | 1+0.1 | 5.2 | 4377 | 33.9 | 162 | 260.1 | 0 | 12582.6 | 4218.2 | 85.9 | 0 | 61733.4 | 21.9 | yes |
| 5.8 | 2 | + $MnSO_4$ + $Na_2S_2O_8$ | 2+1 | 8.6 | 152 | 19.7 | 2.9 | 5.6 | 0 | 8.6 | 25.9 | 9.9 | 0 | 115.9 | 23.7 | yes |
| 5.9 | | + NaOH | | 10.0 | 90 | 0 | 1.2 | 2.4 | 0 | 7.3 | 0.8 | 1.4 | 0 | 53.4 | 34.4 | yes |
| **Analysis done 24.11.** Two-stage treatment: pH adjustment to ca 5 with sodium hydroxide followed by $H_2O_2$ addition, pH adjustment to 8.6, $MnSO_4$ oxidation with peroxide, and final pH adjustment to 10. Reagent concentrations: $H_2O_2$ 3.3%, $MnSO_4$ 10g/l, $Na_2S_2O_8$ 6%, NaOH 0.2M. | | | | | | | | | | | | | | | | |
| 5.4 | 1 | 100ml AMD + $H_2O_2$ | 0.6 | 5.2 | 4158 | 31.6 | 164.6 | 258.5 | 0 | 13538.7 | 4131.3 | 80.6 | 0 | 62759.6 | 32.6 | yes |
| 5.5 | 2 | + MnSO4 + $Na_2S_2O_8$ | 1+0.5 | 8.6 | 71 | 30.1 | 5.2 | 11.9 | 0 | 8.2 | 4417 | 0.5 | 0 | 71.1 | 18.1 | yes |
| 5.6 | | + NaOH | | 10.0 | 58 | 0 | 0 | 2.4 | 0 | 6.2 | 0.5 | 0.1 | 0 | 18.8 | 15.7 | yes |

The analytical wavelengths for each analysed element are shown below:

| | Al | As | Cd | Co | Cr | Cu | Mn | Ni | Pb | Zn | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Wavelength, nm | 396.152 | 188.980 | 214.439 | 238.892 | 267.716 | 327.395 | 257.610 | 231.604 | 220.353 | 213.857 | 238.204 |

## Appendix 6. Results of three-stage treatment tests. Analysed by ALS 20.12.17

| Test No. | Test name | pH | Al, µg/l | As, µg/l | Cd, µg/l | Co, µg/l | Cr, µg/l | Cu, µg/l | Mn, µg/l | Ni, µg/l |
|---|---|---|---|---|---|---|---|---|---|---|
| | **Raw water, ALS results filt.** | 2.8 | 84100 | 14.70 | 176 | 295 | 30.3 | 21900 | 4260 | 71.6 |
| | **Treated water quality, oct 2017** | | 1340 | 1.10 | 1.4 | 0.6 | 1.1 | 15.9 | 148 | 0.3 |
| | **Requirements** | | | 0.50 | 0.25 | | 3.4 | 0.5 | | 4.0 |
| | Unfiltered raw AMD | 2.8 | 87200 | 1.64 | 182 | 286 | 6.0 | 17700 | 3810 | 86.4 |
| | After stage 1 lime addition | 4.2 | 20000 | 1.48 | 174 | 278 | <2.0 | 13300 | 3760 | 78.1 |
| 1 | Test 1 after NaHS | 4.5 | 62700 | 1.60 | 2 | 271 | 5.5 | <1 | 4050 | 81.0 |
| 1 | Test 1 after stage 3 lime | 9.2 | 1930 | 1.36 | <0.05 | 1 | 0.6 | <1 | 482 | 0.6 |
| 2 | Test 2 after NaHS | 4.3 | 66600 | 0.74 | <0.05 | 239 | 5.4 | <1 | 3960 | 79.5 |
| 2 | Test 2 after stage 3 lime | 9.3 | 1190 | 0.91 | <0.05 | 4 | <0.5 | <1 | 1210 | 8.3 |
| | After stage 1 lime addition | 4.6 | 26200 | 9.27 | 170 | 268 | 32.9 | 16900 | 4100 | 81.0 |
| 3 | Test 3 after NaHS | 5.8 | 1590 | 0.83 | <0.05 | 218 | <0.5 | <1 | 3840 | 72.2 |
| 3 | Test 3 after stage 3 lime | 9.2 | 64 | 1.04 | <0.05 | 95 | <0.5 | <1 | 2780 | 52.6 |
| 4 | Test 4 after NaHS | 5.5 | 3120 | 0.63 | <0.05 | 196 | <0.5 | <1 | 3960 | 72.8 |
| 4 | Test 4 after stage 3 lime | 9.1 | 75 | 0.94 | <0.05 | 37 | <0.5 | <1 | 2430 | 45.6 |
| 5 | Test 5 after NaHS | 5.4 | 2140 | 0.65 | <0.05 | 186 | <0.5 | <1 | 3960 | 70.9 |
| 5 | Test 5 after stage 3 lime | 9.4 | 63 | 1.01 | <0.05 | 15 | <0.5 | <1 | 2000 | 36.6 |
| | After stage 1 lime addition | 5.2 | 2540 | 0.78 | 177 | 279 | <0.9 | 8630 | 3680 | 85.2 |
| 6 | Test 6 after NaHS | 6.6 | 82 | 0.63 | 0.08 | 236 | <0.5 | <1 | 3950 | 79.3 |
| 6 | Test 6 after stage 3 lime | 9.3 | 5 | 0.69 | <0.05 | 113 | <0.5 | <1 | 2880 | 57.8 |
| 7 | Test 7 after NaHS | 6.7 | 289 | 0.59 | <0.05 | 1 | <0.5 | <1 | 3790 | 43.3 |
| 7 | Test 7 after stage 3 lime | 9.4 | 49 | 0.57 | <0.05 | 0.3 | <0.5 | <1 | 2740 | 32.1 |

| Test No. | Test name | pH | Pb, µg/l | Zn, µg/l | Fe, µg/l | S, mg/l | SO4, mg/l | U, µg/l | Hg, µg/l | Si, µg/l |
|---|---|---|---|---|---|---|---|---|---|---|
| | **Raw water, ALS results filt.** | 2.8 | 251 | 78000 | 141000 | 921 | 2780 | 19.1 | 0.02 | 17900 |
| | **Treated water quality, oct 2017** | | 0.25 | 73 | 92 | | | | | |
| | **Requirements** | | 1.2 | 6 | | | | 8.6 | 0.07 | |
| Unfiltered raw AMD after sedimentation | | 2.8 | 117 | 83600 | 4200 | 1010 | 2860 | 18.3 | <0.02 | 19300 |
| | Limed water for tests 1-2 | 4.2 | 63 | 81900 | 2330 | 1000 | 2700 | 13.7 | <0.02 | 18600 |
| 1 | Test 1 after NaHS | 4.5 | 0.4 | 57100 | 4320 | 933 | 2790 | 17.6 | <0.02 | 17300 |
| 1 | Test 1 after stage 3 lime | 9.2 | <0.2 | 18 | <4.0 | 935 | 2670 | 1.1 | <0.02 | 633 |
| 2 | Test 2 after NaHS | 4.3 | <0.2 | 12 | 4210 | 930 | 2640 | 17.7 | <0.02 | 17200 |
| 2 | Test 2 after stage 3 lime | 9.3 | <0.2 | <2 | <4.0 | 946 | 2610 | 7.8 | <0.02 | 2300 |
| | Limed water for tests 3-5 | 4.6 | 315 | 79400 | 3070 | 980 | 2470 | 23.3 | <0.02 | 16500 |
| 3 | Test 3 after NaHS | 5.8 | <0.2 | 1420 | 1510 | 933 | 2730 | 6.4 | <0.02 | 13600 |
| 3 | Test 3 after stage 3 lime | 9.2 | 0.4 | 12 | 11 | 933 | 2720 | 6.1 | <0.02 | 11200 |
| 4 | Test 4 after NaHS | 5.5 | <0.2 | 48 | 1690 | 942 | 2840 | 8.1 | <0.02 | 13500 |
| 4 | Test 4 after stage 3 lime | 9.1 | <0.2 | <2 | 5 | 935 | 2510 | 6.3 | <0.02 | 10400 |
| 5 | Test 5 after NaHS | 5.4 | <0.2 | 153 | 1530 | 940 | 3060 | 6.9 | <0.02 | 13200 |
| 5 | Test 5 after stage 3 lime | 9.4 | <0.2 | <2 | <4.0 | 957 | 2820 | 5.5 | <0.02 | 10400 |
| | Limed water for tests 6-7 | 5.2 | 18 | 79800 | 365 | 989 | 2770 | 4.9 | <0.02 | 13300 |
| 6 | Test 6 after NaHS | 6.6 | <0.2 | 17500 | <4.0 | 939 | 2530 | 3.5 | <0.02 | 11700 |
| 6 | Test 6 after stage 3 lime | 9.3 | <0.2 | 42 | <4.0 | 933 | 2530 | 2.0 | <0.02 | 7850 |
| 7 | Test 7 after NaHS | 6.7 | <0.2 | <2 | 12 | 928 | 2810 | 4.6 | <0.02 | 12000 |
| 7 | Test 7 after stage 3 lime | 9.4 | <0.2 | <2 | <4.0 | 939 | 2520 | 2.5 | <0.02 | 11500 |

Cells coloured in pink indicate values below the proposed discharge requirements.

Samples from No. 1, 2, 7 and 14 were analysed for total concentrations. The analysis was done after diluting 12ml samples with 1.2 ml ultrapure nitric acid and treating it in autoclave. ICP-SFMS (inductively coupled plasma sector field mass spectrometry) was used for determination of As, Cr, Cu, Mn, Pb, and U. ICP-AES was used for determination of Fe, S, Si, Al, Cd, Co, Ni, and Zn. Mercury was determined with atomic fluorescence spectrometry (AFS).

Other samples were analysed for dissolved metal concentrations, i.e. they were filtered through a 0.45 µm filter prior to being sent for analysis. These samples were not digested prior to analysis. ICP-SFMS (inductively coupled plasma sector field mass spectrometry) was used for determination of Fe, Al, As, Cd, Co, Cr, Cu, Pb, Ni, and U. ICP-AES was used for determination of S, Si, Mn, and Mg. Mercury was determined with atomic fluorescence spectrometry (AFS).

Analysis with ICP-SFMS has been done according to SS EN ISO 17294-1, 2 (mod) and EPA method 200.8 (mod). Analysis with ICP-AES has been done according to SS EN ISO 11885 (Mod) and EPA Method 200.7 (Mod). Hg analysis with AFS has been done according to SS EN ISO 17852. Sulfate content was measured according to CZ_SOP_D06_02_068 (CSN ISO 10304-1, CSN EN 16192) Determination of dissolved fluoride, chloride, nitrite, bromide, nitrate and sulfate by ionic liquid chromatography and determination of nitrite nitrogen and nitrate nitrogen and sulfate sulfur by calculation from measured values.

## Appendix 7. Results of Fenton and $MnSO_4$ oxidation tests. Analysed by ALS 12.12.17

| Test No. | Test name | pH | Al, µg/l | As, µg/l | Cd, µg/l | Co, µg/l | Cr, µg/l | Cu, µg/l | Mn, µg/l | Ni, µg/l |
|---|---|---|---|---|---|---|---|---|---|---|
| | **Raw water, ALS results filt.** | 2.8 | 84100 | 14.70 | 176.00 | 295.00 | 30.30 | 21900.0 | 4260 | 71.6 |
| | **Treated water quality, oct 2017** | | 1340 | 1.07 | 1.44 | 0.56 | 1.11 | 15.9 | 148 | 0.3 |
| | **Requirements** | | | 0.50 | 0.25 | | 3.40 | 0.5 | | 4.0 |
| | After lime neutralization | 9.3 | 3030 | 0.90 | 1.21 | 0.19 | 2.24 | 3.9 | 63 | <0.5 |
| 1 | 50 mg/l Mn + 1:2 $H_2O_2$ | 9.7 | 79 | 0.60 | <0.05 | 0.09 | 1.96 | 2.1 | 15 | <0.5 |
| 2 | 50 mg/l Mn + 1:3 $H_2O_2$ | 9.3 | 349 | 0.60 | <0.05 | 0.08 | 1.94 | 1.1 | 109 | <0.5 |
| 3 | CP 1 125 mg/l Mn + 1:2.25 $H_2O_2$ | 9.1 | 203 | 0.75 | <0.05 | 0.11 | 1.65 | <1.0 | 5730 | <0.5 |
| 4 | CP 2 125 mg/l Mn + 1:2.25 $H_2O_2$ | 8.9 | 188 | 0.54 | 0.05 | 0.32 | 1.59 | 1.2 | 44800 | <0.5 |
| 5 | 200 mg/l Mn + 1:2 $H_2O_2$ | 9 | 84.8 | 0.80 | 0.06 | 0.59 | 1.43 | <1.0 | 77000 | 1.0 |
| 6 | 200 mg/l Mn + 1:3 $H_2O_2$ | 8.9 | 67 | 0.73 | 0.06 | 0.61 | 1.23 | <1.0 | 84100 | 0.6 |
| 7 | 50 mg/L Mn + $Ca(OH)_2$ | 9.5 | 3 | 0.82 | <0.05 | <0.05 | 0.66 | <1.0 | 2970 | 0.6 |
| 8 | 125 mg/l Mn + $Ca(OH)_2$ | 9.4 | <2 | 0.66 | <0.05 | <0.05 | <0.50 | <1.0 | 27000 | <0.5 |
| | After lime neutralization | 9 | 2910 | 0.90 | 1.25 | 0.23 | 1.72 | 4.2 | 122 | <0.5 |
| 1 | 30 mg/L Fe + 1:2 $H_2O_2$ | 9.5 | 683 | 0.51 | <0.05 | 0.67 | 0.791 | 1.5 | 2.54 | 0.8 |
| 2 | 30 mg/L Fe + 1:2.5 $H_2O_2$ | 9.3 | 807 | 0.54 | <0.05 | 0.63 | 1.63 | 1.1 | 1.37 | 1.0 |
| 3 | CP 1 65 mg/L Fe + 1:2.25 $H_2O_2$ | 9.5 | 605 | 0.57 | <0.05 | 0.17 | 1.34 | <1.0 | 1.31 | 1.6 |
| 4 | CP 2 65 mg/L Fe + 1:2.25 $H_2O_2$ | 9.3 | 440 | <0.50 | <0.05 | 0.13 | 0.932 | <1.0 | 1.31 | 1.0 |
| 5 | CP 3 65 mg/L Fe + 1:2.25 $H_2O_2$ | 9.3 | 492 | 0.80 | <0.05 | 0.25 | 0.754 | <1.0 | 0.52 | 1.4 |
| 6 | 100 mg/L Fe + 1:2 $H_2O_2$ | 9.4 | 57 | <0.50 | <0.05 | 0.16 | 1.54 | <1.0 | 0.60 | 1.3 |
| 7 | 100 mg/L Fe + 1:2.5 $H_2O_2$ | 9.3 | 353 | 0.54 | <0.05 | 0.13 | 1.22 | 1.2 | 0.80 | 1.0 |

| Test No. | Test name | pH | Pb, µg/l | Zn, µg/l | Fe, µg/l | S, mg/l | SO4, mg/l | U, µg/l | Hg, µg/l | Si, µg/l |
|---|---|---|---|---|---|---|---|---|---|---|
| | **Raw water, ALS results filt.** | 2.8 | 251.0 | 78000 | 141000.0 | 921 | 2780 | 19.10 | 0.02 | 17900 |
| | **Treated water quality, oct 2017** | | 0.3 | 73 | 92.0 | | | | | |
| | **Requirements** | | 1.2 | 6 | | | | 8.60 | 0.07 | |
| | After lime neutralization | 9.3 | <0.2 | 4 | <4.0 | 914 | 2870 | 0.31 | 0.023 | 402 |
| 1 | 50 mg/l Mn + 1:2 $H_2O_2$ | 9.7 | <0.2 | <2 | <4.0 | 970 | 2860 | 0.12 | <0.02 | 606 |
| 2 | 50 mg/l Mn + 1:3 $H_2O_2$ | 9.3 | <0.2 | <2 | <4.0 | 962 | 3010 | 0.12 | <0.02 | 543 |
| 3 | CP 1 125 mg/l Mn + 1:2.25 $H_2O_2$ | 9.1 | <0.2 | <2 | <4.0 | 1010 | 2950 | 0.07 | <0.02 | 372 |
| 4 | CP 2 125 mg/l Mn + 1:2.5 $H_2O_2$ | 8.9 | <0.2 | <2 | <4.0 | 994 | 3140 | 0.09 | <0.02 | 266 |
| 5 | 200 mg/l Mn + 1:2 $H_2O_2$ | 9 | 0.4 | <2 | <4.0 | 1030 | 3140 | 0.11 | <0.02 | 272 |
| 6 | 200 mg/l Mn + 1:3 $H_2O_2$ | 8.9 | <0.2 | <2 | <4.0 | 1060 | 3330 | 0.07 | <0.02 | 280 |
| 7 | 50 mg/L Mn + $Ca(OH)_2$ | 9.5 | <0.2 | <2 | 4.3 | 921 | 2670 | 0.04 | <0.02 | 285 |
| 8 | 125 mg/l Mn + $Ca(OH)_2$ | 9.4 | <0.2 | <2 | <4.0 | 886 | 2580 | 0.02 | <0.02 | <200 |
| | After lime neutralization | 9 | <0.2 | 4 | <4.0 | 921 | 2690 | 0.41 | 0.027 | 397 |
| 1 | 30 mg/L Fe + 1:2 $H_2O_2$ | 9.5 | <0.2 | <2 | 26.2 | 948 | 3020 | <0.01 | <0.02 | <200 |
| 2 | 30 mg/L Fe + 1:2.5 $H_2O_2$ | 9.3 | <0.2 | <2 | 48.5 | 958 | 3200 | <0.01 | <0.02 | <200 |
| 3 | CP 1 65 mg/L Fe + 1:2.25 $H_2O_2$ | 9.5 | <0.2 | <2 | 31.3 | 960 | 3070 | <0.01 | <0.02 | <200 |
| 4 | CP 2 65 mg/L Fe + 1:2.25 $H_2O_2$ | 9.3 | <0.2 | <2 | 47.1 | 984 | 3130 | <0.01 | <0.02 | <200 |
| 5 | CP 3 65 mg/L Fe + 1:2.25 $H_2O_2$ | 9.3 | <0.2 | <2 | 23.0 | 1000 | 2730 | <0.01 | <0.02 | <200 |
| 6 | 100 mg/L Fe + 1:2 $H_2O_2$ | 9.4 | <0.2 | <2 | 28.9 | 1020 | 3010 | <0.01 | <0.02 | <200 |
| 7 | 100 mg/L Fe + 1:2.5 $H_2O_2$ | 9.3 | <0.2 | <2 | 33.5 | 980 | 3240 | <0.01 | <0.02 | <200 |

Prior to analysis samples have been acidified with 1 ml ultrapure nitric acid per 100 ml. Analysis with ICP-SFMS has been done according to SS EN ISO 17294-1, 2 (mod) and EPA method 200.8 (mod). Analysis with ICP-AES has been done according to SS EN ISO 11885 (mod) and EPA Method 200.7 (mod). Hg was analyzed with AFS according to SS EN ISO 17852. Sulfate content was analyzed by method CSN ISO 10304-1, CSN EN 16192.

# Appendix 8. Chemical reagents used during experimental work

*Table 1. Analytical grade reagents used in the experimental work.*

| Name | Chemical formula | Molecular weight, g/mol | Purity | Manufacturer |
|---|---|---|---|---|
| Calcium hydroxide | $Ca(OH)_2$ | 74.09 | 95% | Alfa Aesar |
| Iron(II) sulfate heptahydrate | $FeSO_4*7H_2O$ | 278.02 | analytical grade | Merck KGaA |
| Magnesium hydroxide | $H_2MgO_2$ | 58.33 | 99.7% | VWR International |
| Manganese(II) sulfate monohydrate | $MnSO_4*H_2O$ | 169.02 | 98.0-101.0% | Alfa Aesar |
| Sodium hydroxide | HNaO | 40.00 | >98% | GPR RECTAPUR |
| Sodium peroxodisulfate | $Na_2S_2O_8$ | 238.10 | ≥98% | Sigma-Aldrich |
| Sodium sulphide about trihydrate | $Na_2S.{\sim}3H_2O$ | 78.04 | 61% | VWR International |
| Sodium hydrosulfide hydrate | $NaHS{\sim}3.3H_2O$ | 56.06 | na | Honeywell Fluka |
| Sulphuric acid | $H_2SO_4$ | 98.07 | 95% | VWR International |
| TMT15® 1,3,5-triazine-2,4,6(1H,3H,5H)-trithione, tridisodium salt | | | | Evonik Degussa GmbH |

*Table 2. Industrial grade regents used in the experimental work.*

| Name | Chemical formula | Molecular weight, g/mol | Manufacturer |
|---|---|---|---|
| Calcium carbonate | $CaCO_3$ | 100.1 | Labassco |
| Calcium hydroxide | $Ca(OH)_2$ | | na |
| Hydrogen peroxide | $H_2O_2$ | | na |
| Potassium permanganate | $KMnO_4$ | 158.03 | Labassco |
| Sodium hydrosulfide | NaHS | | na |
| Sodium hypochlorite | NaClO | | na |